COLLOID JOURNAL (USSR)

Volume XVI, Number 3

May-June, 1954

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU
152 WEST 42 ND ST., NEW YORK 18, N.Y.

—An agency for the interpretation of international knowledge—

Colloid Journal (U.S.S.R.) in English Translation, May-June, 1954

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COLLOID JOURNAL

Journal of Theoretical and Applied Physics and Chemistry of Colloids

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Publication of the Academy of Sciences of the U. S. S. R.

IN ENGLISH TRANSLATION

Copyright, 1954

CONSULTANTS BUREAU

152 West 42nd Street

New York 18, N. Y.

Printed in the United States

Annual subscription $ 80.00
Single issue 20.00

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COAGULATION OF POLYSTYRENE LATEXES BY ELECTROLYTES

E. M. Aleksandrova and P. V. Mochalov

Polystyrene latexes are highly dispersed colloidal systems with considerable aggregative stability. Polystyrene latexes obtained by the widely used method of emulsion polymerization can be kept for a long time without change. Aging occurs in very dilute latexes with a weight concentration of about 0.2 g/l. In this respect, these systems differ from the resin hydrosols studied previously in our laboratory [1]. Sols of rosin, mastic, gamboge, Novolak,** and other resins age rapidly, and the autocoagulation mechanism differs according to the degree of polydispersity of the sol and the solubility of the resin in the dispersion medium. Certain sols, protected by gelatin against aggregation, aged when the solubility of the resin was increased by heat or by addition of an organic solvent. The kinetics of aggregation and supercondensation follow different curves. The aging of dilute polystyrene latexes follows the aggregation curve, but is not well-defined.

Great practical interest is presented by electrolytic coagulation of latexes, which is described briefly in this paper.

The course of coagulation was observed by increase of the optical density of the latex, due to a lowering of the degree of dispersion in the initial stage of coagulation while kinetic stability is retained. The optical density was measured with the aid of a universal photometer with a set of calibrated light filters. At latex concentrations below 1 g/l a direct proportionality was established between D_λ/d and c (D_λ is the optical density; c is the weight concentration; d is the thickness of the layer). From the nature of the relationship of D_λ to the wavelength λ, dilute polystyrene latexes may be classed as "white sols". The validity of the Equation

$$D_\lambda = K\lambda^{-n},$$

was confirmed, where n is a factor which varies steadily with the degree of dispersion.

With the use of published studies of the optical properties of white sols [2, 3], it is possible to determine the particle size. We established the empirical relationship

$$F \simeq \beta w^{\alpha},$$

where F is the relative increment of the optical density caused by aging or by addition of coagulants; w is the relative increment of the particle volume; β and α are constants.

The optical method for the determination of the degree of dispersion of latexes was described in detail in one of our papers [4] and in the dissertation by P. V. Mochalov (Mendeleev Institute of Chemical Technology, Moscow, 1952). The appropriate calibration curve was plotted for the rapid determination of the degree of dispersion of the latexes.

Two materials were used for the coagulation experiments: production latex stabilized with "MK", obtained from the factory, and a laboratory latex made by us with a stabilizer known as "Nekal". In the technical literature this name is replaced by "Wetting agent NB". It is not considered an individual chemical substance, and therefore, it is more correct to refer not to the Na salt of butylnaphthalene sulfonic acid, but to the coexisting Na salts of sulfonic acids of butylnaphthalene derivatives obtained as a result of the synthesis. As it is a colloidal electrolyte with a surface-active anion, "Wetting agent NB" is an excellent stabilizer for various disperse systems. Various methods may be used for studying micelle formation in aqueous solutions, including the optical [5] and conductometric methods.*

The electrical conductivity of aqueous solutions of "Wetting agent NB" changes anomalously with increase of concentration (electrolyte impurities should be removed from the stabilizer by reprecipitation from absolute alcohol, for which the Soxhlet apparatus may conveniently be used.). Graphs for c against κ and for c against κ/c were obtained, where c is the weight concentration and κ the conductivity. The second graph corresponds to a curve which shows the relationship between concentration and equivalent conductivity. In view of the uncertainty

* The electrical conductivity of "Wetting agent NB" was studied by student Zagraevskaya, and reported at the 1952 scientific conference.

** Lacquer resins prepared from phenol or cresol and aldehydes. (Publisher.)

concerning the chemical nature of the stabilizer, it was not possible to use such concepts as molecular weight and molecular concentration. The curves for χ/c were a repetition of the curves obtained by McBain [6], Pospelova and Markina [7], and other authors who studied micelle formation in solutions of anion-active colloidal electrolytes.

Colloidal electrolytes are good stabilizers of disperse systems because surface activity is accompanied by capacity for micelle formation. The adsorptional layer of such a stabilizer ensures not only an ionic solvation envelope, but, what is still more important, also the structural-mechanical properties of the system.

The adsorption of "Wetting agent NB" on latex particles was shown experimentally. Structure formation was confirmed by rheological curves for p against $1/z$ where p is the pressure difference and z is the efflux time measured with an Ubbelohde viscosimeter. It should be noted that structure formation is aided by the addition of small quantities of electrolyte (NaCl). In view of the possibility of the existence of two factors in latex stabilization, and also of the specific effect of different electrolytes on latex stability, we studied the ξ-potential of latexes with varying concentrations of the disperse phase and in presence of a number of salts, by the electrophoretic method.* It was shown that the ξ-potential, which had negative sign, decreases with dilution of the latex.

This may be explained on the assumption of desorption of the potential-determining ions from the surfaces of particles. The former may be monomeric stabilizer ions which exist in dynamic equilibrium with the micelles. In the presence of univalent cations (NaCl, KCl, NH_4Cl), the ξ-potential falls to 10-15 mV, and the latex does not coagulate. This confirms the preponderant significance of the structural-mechanical factor in stabilization. It was stated above that the addition of small amounts of NaCl favors structure formation. Precipitation of the latex requires amounts of NaCl which are characteristic not of coagulation, but of salting-out. The cations are placed in a lyotropic series according to their ability of lowering the ξ-potential.

The nature and the laws of electrolytic coagulation greatly depend on the techniques used in the study of this process, which require standardization. The kinetics of coagulation, like the kinetics of aging, may be represented by the empirical equation

$$F = bz^m,$$

where F is the increase in the optical density in time, z, relative to the original value:

$$F = \frac{D_z - D_0}{D_0}$$

The constant m is practically independent of the coagulant concentration, if the conditions of the experiment are constant. The constant b, which depends on the coagulation rate, changes sharply with electrolyte concentration. Table 1 shows the increase of the constant b on addition of increasing amounts of electrolytes such as NaCl and $CaCl_2$.

TABLE 1

Effect of Electrolyte Concentration on the Coagulation of Polystyrene Latex.

NaCl		$CaCl_2$	
c_e mM/l	b	c_e mM/l	b
3.2	0.1	0.164	0.06
3.43	0.15	0.218	0.32
3.6	0.205	0.246	0.84
4.0	0.46	0.273	1.98
4.4	1.0	0.328	7.0
		0.357	7.6

When plotted in logarithmic coordinates, the kinetics of coagulation may be represented by a series of straight lines (the points fit reasonably well).

With the aid of the empirical laws found, it was possible, without much difficulty, to calculate the time φ in the course of which the total number of particles in the coagulating latex is halved. The time of "half-coagulation" so obtained is compared with the theoretically calculated value φ_0 which represents the time necessary to halve the number of particles in a similar sol which is fully stabilized.

The value of φ_0 may be calculated from the Smoluchowsky Equation [8]:

$$\varphi_0 = \frac{3}{4} \cdot \frac{N\eta}{RTv_0}.$$

If the particle diameter is 77 mμ and the concentration is expressed in g/ml, then:

$$\varphi_0 = \frac{0.47 \cdot 10^{-4}}{c} \text{ sec.}$$

* Student I. Kulyulin participated in work on ξ-potential measurements.

The value of φ_0 is calculated on the assumption of 100% effective collisions between the particles of the coagulating sol. Experimentally, a greater value of φ is found, which corresponds to the retention of a certain measure of aggregative stability and correspondingly lower effectiveness of collisions. In Smoluchowsky's theoretical derivations, the effectiveness of collisions is mathematically expressed by the coefficient ϵ which varies between 0 and 1.

We used the reciprocal value $1/\epsilon$ which shows the extent to which a given latex is removed from the fully destabilized state [9]. Comparison of the coagulation rates of the same sol, partly and fully destabilized gives a measure of the aggregative stability of a given system. We used the time of half-coagulation φ, which could be calculated from the experimental data:

$$\frac{\varphi}{\varphi_0} = \frac{1}{\epsilon} .$$

The greater the aggregative stability of the sol, the greater is $1/\epsilon$; minimum values of $1/\epsilon = 1$.

TABLE 2

Effect of Coagulant Concentration on the Stability of Polystyrene Latexes.

NaCl			$CaCl_2$		
$c_e \frac{mM}{l}$	$\frac{1}{\epsilon} \cdot 10^{-2}$	$\log\frac{1}{\epsilon}$	$c_e \frac{mM}{l}$	$\frac{1}{\epsilon} \cdot 10^{-2}$	$\log\frac{1}{\epsilon}$
3.2	210	4.322	0.164	187	3.272
3.6	69	3.81	0.246	5.75	2.76
4.4	7.75	2.89	0.273	1.87	2.272
4.8	1.95	2.29	0.283	1.115	2.048
5.21	0.87	1.94	0.357	0.316	1.5

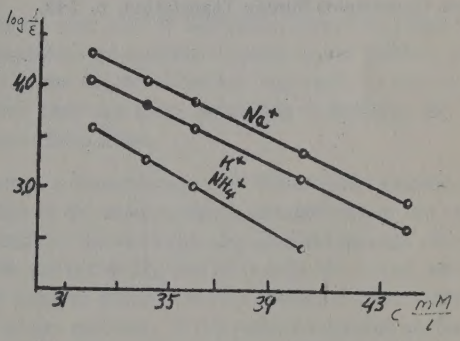
The value of $1/\epsilon$ falls sharply with increasing concentration of the coagulant electrolytes.

From a comparison of the concentrations of different coagulants which correspond to a given value of $1/\epsilon$ (for example, $1/\epsilon = 250$), it is possible to judge the coagulating power of ions. The cations investigated by us form a series in the order of their coagulating action which does not differ from the lyotropic series mentioned above. Over a certain range of concentrations of the coagulant electrolytes $\log 1/\epsilon$ decreases linearly with coagulant concentration (see Figure).

The aggregative stability falls with increasing dilution of the latex, as is seen clearly from Table 3.

The stability of both the latexes studied is sufficient for their use in bonding fibrous materials.

Thus, we have a certain measure of aggregative stability, which has a number of advantages over such values as the frequently cited coagulation thresholds. The value of $1/\epsilon$ does not depend on a number of factors which cause discrepancies in the experimentally determined coagulation thresholds. The absence of periods of rapid coagulation (when the effect ceases to depend on the concentration of coagulant) and the high values of $1/\epsilon$ (Table 2) indicate the high stability of polystyrene latexes, which is possible in presence of a structural-mechanical stabilization factor.



Effect of coagulant concentration on the aggregative stability of polystyrene latex (the values of c_e are multiplied by 10).

SUMMARY

1. A study was made of the aggregative stability of polystyrene latexes obtained in presence of anion-active stabilizers ("Wetting agent NB" and Emulsifier MK).

2. Long periods of slow coagulation occur during the electrolytic coagulation of the latexes.

3. The high stability of the latexes depends significantly on the structural-mechanical properties of the adsorbed stabilizer layers.

4. The applicability is shown of the experimental data on coagulation kinetics to the comparative evaluation of the aggregative stability of polystyrene latexes, in agreement with the slow coagulation theory of Smoluchowsky and Deryagin.

TABLE 3

Effect of Dilution of the Latex on its Aggregative Stability

Dilution	$\frac{1}{\epsilon} \cdot 10^{-2}$	Dilution	$\frac{1}{\epsilon} \cdot 10^{-2}$
8	84.0	16	57.4
10	73.2	20	51.2
12	67.0	30	42.2

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Received July 10, 1953.

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*See Consultants Bureau Translation, p. 149.

**See Consultants Bureau Translation, p. 243.

EFFECT OF STRUCTURE FORMATION ON THE PROPERTIES OF KAOLIN

E. A. Galabutskaya

The properties of the clay-water system may vary considerably according to the nature of the interaction between the clay particle surfaces and the water molecules, and the degree of mutual attraction between the particles. Two types of water are distinguished in hydrophilic disperse systems: water firmly bound with the colloidal particles, and water which serves only as the dispersion medium in which the micelles exist [1]. Similarly, Lebedev [2] distinguishes two kinds of water in clays: bound water, held on the particle surfaces by molecular attraction forces, and free water, which is not subject to the action of molecular forces and which is the dispersion medium in the clay-water system.

The water molecules which surround the mineral particles of moist clay are firmly bound to the particle surfaces by the action of considerable forces of attraction. These layers of water, which form the so-called firmly bound water, in their turn produce orientation in the adjacent molecules of water, which constitute the so-called loosely bound water [3]. The firmly and the loosely bound water together comprise the bound water.

The thickness of the layer of bound water in clay minerals varies in wide limits – from thousandths to tenths of a micron. Clay minerals of the montmorillonite group have particularly high water-binding power [4].

The hydrophily of kaolin, which is determined by the amount of water adsorptionally bound on its particle surfaces, is less than that of other clay minerals. Thus, the amount of bound water found by Dumansky [5] is 2.15% for Glukhovets' kaolin, and 7.08% for Chasovyarsky clay.

The mutual attraction which causes clay particles to cohere may lead to different types of structure formation, the nature of which depends on the existence and the thickness of the aqueous coating on the particle surfaces. The degree of aggregation of clay particles varies with changes in the degree of surface hydration, in relation to the intensity of the coagulation effect. As the particles join together, they can form, according to Rebinder [6], both loose, strongly hydrated aggregates, and also more or less compact formations.

Reagents which increase the surface hydration of the particles disperse clay into the smallest primary crystals surrounded by a solvation coating, the thickness of which depends on the mineralogical composition of the clay. The formation of structures in such a system occurs as the result of contact between the clay leaflets through these coatings. The amount of water bound in the solvation coating on the surface of the particles depends on the presence of a stabilizing reagent in the system. The packing density of the disperse phase in such a system is determined by the thickness of the solvation coating on the surface of the crystals of the mineral. If the surface becomes partially hydrophobic, separate particles of the clay cohere by forces of molecular attraction at points where the hydration envelope is thin or broken. The cells of the structure so formed may retain considerable amounts of the dispersion medium [6].

As the amount of dehydrating agent increases, the particles join by considerable portions of their surfaces, forming aggregates which readily separate from the dispersion medium. Variations in the packing density of the clay particles with different degrees of surface hydration and also with different amounts of water retained in the cells of the structure as the result of structure formation should modify sharply the properties of the clay-water system. Variations should be found in such properties of clay as plasticity, limiting shear stress, water permeability, rate of drying, and also viscosity and rate of filtration of its suspensions.

In factory practice, in the plastic method of forming, the working state of a plastic ceramic mass is generally determined by its moisture content. For different types of products, masses are used the moisture content of which lies within fairly narrow limits [7, 8]. However, the resistence of the mass to mechanical forces during forming, and its moisture content, may vary considerably as the result of structure formation in the kaolin which is contained in the mass.

Figures 1, 2, and 3 show the results of moisture determination on kaolins obtained after filtration, under the same conditions, of suspensions containing different amounts of reagents which vary the degree of surface

hydration of kaolin particles. The same figures show results of measurements of the sedimentational volumes obtained in the kaolin suspensions with these additions after standing. Glukhovets' kaolin, enriched in distilled water under laboratory conditions, was used in the experiments. The nature of structure formation in the clay was varied by the addition to its suspensions (density 1.34) of different amounts of water glass and lime.

In water, particles of kaolin break up into separate crystalline particles less easily than is the case for other clay minerals. Kaolins generally have, for this reason, a lower specific surface than clays which contain such minerals as montmorillonite or monothermite. Thus, according to Dumansky's data [5], the specific surface of Glukovets' kaolin is $\sim$38 m^2/g, and that of Chasovyarsky clay is 223 m^2/g. The specific surface of bentonite, according to Gapon [9], is 1300 m^2/g.

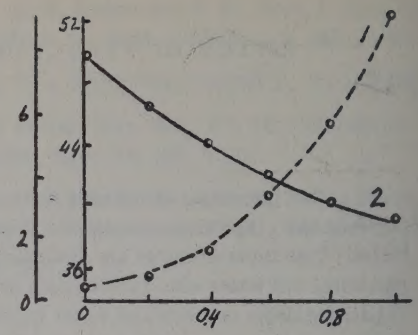

Figure 1. Effect of additions of water glass: 1 - on the moisture content of filtered kaolin, 2 - on the sedimentational volume of its suspensions.

In peptized suspensions the relatively large particles of kaolin, in settling out, form dense precipitates with a low sedimentational volume. The aqueous envelopes, which do not hinder the slippage of particles against each other, prevent their cohesion into loose aggregates. The sedimentational volume of the suspensions was determined in cylinders 15 mm diameter and 400 cm high. After five days' standing, peptized suspensions contained a dense precipitate above which was a layer of turbid liquid containing smaller particles, which did not settle out in this period. In the type of kaolin studied these particles comprised 4.6%.

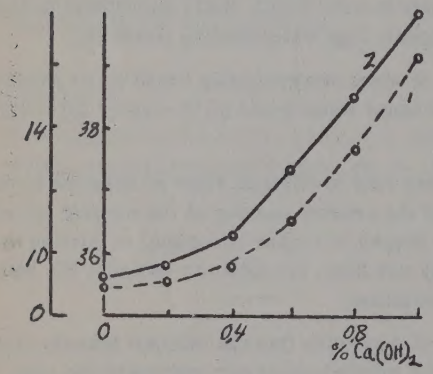

Figure 2. Effect of additions of lime: 1 - on the moisture content of filtered kaolin, 2 - on the sedimentational volume of its suspensions.

The sedimentational volumes of the precipitates increase with addition of lime. The looser structure of the precipitates obtained in this case is due to the direct joining of kaolin particles, with formation of cells filled with the dispersion medium. A similar increase in the sedimentational volumes is observed also on the addition of lime to suspensions prepared with distilled water, without peptizing electrolyte.

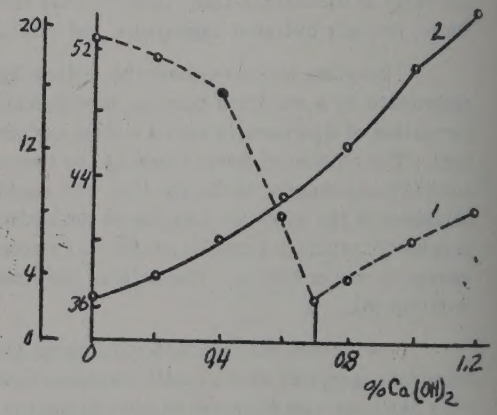

Figure 3. Effect of additions of lime: 1 - on the moisture content of filtered kaolin, 2- on the sedimentational volume of suspensions (suspension previously stabilized).

Structure formation of an analogous nature is observed in masses obtained after filtration of suspensions. A peptized suspension forms a dense precipitate with a low active porosity on the filter. This hinders filtration and is the cause of increased moisture in the filtered material. However, although the total moisture content of the whole filtered mass is high, the moisture content of the kaolin immediately at the filtering surface is not great. Thus, for suspensions containing 1.0% water glass, the respective moisture contents are 59.2 and 31.2%.

On the addition of lime to the peptized kaolin, the density of the precipitate on the filter decreases, the rate

of filtration increases, and the total moisture content of the filtered kaolin decreases. However, for certain amounts of added lime, as the viscosity of the suspensions increases, the moisture content of the filtered material begins to increase, because the kaolin particles form cells filled with the dispersion medium by cohering together as the surface becomes hydrophobized. As Figure 2 shows, the addition of lime to suspensions without peptizing agent also results in an increase in the moisture content of the filtered material.

Similar variations of moisture content with changes in the nature of structure formation are also observed in kaolin masses of normal consistency. Moisture content variations in masses of normal consistency on the addition of water glass and lime to kaolin are shown in Table 1.

TABLE 1
Moisture Content of Kaolin on Additions of Water Glass and Lime

Type and amount of electrolyte added	Water content, %, in mass of normal consistency
Glukhovets kaolin without electrolyte	39.8
Glukhovets kaolin peptized with water glass (1% on the weight of the kaolin)	37.1
Glukhovets kaolin, coagulated with lime (1% on the weight of the kaolin)	40.2
Glukhovets kaolin first peptized with water glass (1% on the weight of the kaolin) and then coagulated with lime (1.4% on the weight of the kaolin)	41.0

In the molding of ceramic articles, condensation deformation takes place, accompanied by a decrease in the volume of the mass. Thus, a mass cast in a plaster mold gives up part of its moisture content to the mold, is condensed, shrinks, and can therefore be easily detached from the mold.

The rate at which the plaster mold removes water from the article molded in it, under equal conditions of porosity and moisture content of the mold, and of temperature, depends on the rate of transfer of water in the mass, or the water permeability of the mass. Similarly, the uniformity of densification of the mass which passes through the compressing head of the press will be determined by the rate of filtration of water through the mass.

As was established by the experiments of a number of workers [10, 11], the movement of water in sands and clays may be regarded as a parallel-streamed, laminary flow in a porous medium. The rate of densification of clay, within certain limits, is directly proportional to its filtration coefficient, the value of which depends on the mechanical composition, porosity, and structure of the clay. The presence of layers of bound water on the clay particle surfaces retards the process, as free filtration in these clays occurs only through the pores fillled with non-bound water. Filtration of bound water is hindered by the increased viscosity and appreciable resilience to shear of this water. The viscosity of bound water depends on the thickness of its layer, thus, for a layer thickness of 0.16 μ, $\eta \approx 0.01$ poise, and for a thickness of 0.02 μ, $\eta = 0.045$ poise [12]. The filtration coefficient for kaolin was determined in a compression filter apparatus, under a load of 1.5 kg/cm^2 which caused filtration of water from the pores of the material. The results are shown in Table 2. Table 2 shows that as the clay becomes less hydrophilic, its filtration coefficient increases.

TABLE 2
Filtration Coefficient for Kaolin, Peptized by Water Glass and Coagulated with Lime

Type and amount of electrolyte added	Filtration coefficient in m/day
Glukhovets kaolin without electrolyte	$0.66 \cdot 10^{-4}$
Glukhovets kaolin peptized with water glass (1% on the weight of the kaolin)	$0.30 \cdot 10^{-4}$
Glukhovets kaolin coagulated with lime (1% on the weight of the kaolin)	$0.25 \cdot 10^{-3}$
Glukhovets kaolin first peptized with water glass (1% on the weight of the kaolin) and then coagulated with lime (1.4% on the weight of the kaolin).	$0.10 \cdot 10^{-3}$

In the manufacture of ceramic articles, the mass is subjected to mechanical forces of various kinds, which ensure the necessary treatment of the mass and confer the required shape to it. The nature of structure formation in the system should affect the molding properties of the mass, its capacity for deformation and condensation in the molding process. Differences in the packing density of the particles, variations in the frictional forces between them, and also different degrees of cohesion between the structural elements of the mass, determine the forces necessary for its deformation during the molding process.

Under the action of applied forces both residual, structural deformations and elastic, reversible deformations occur in the clay mass [13]. Structural deformations in the mass arise in the presence of forces which exceed

the cohesion force between its particles. The separate crystalline elements of the mass, or their aggregates, become displaced in the process, and come in contact with new structural elements. As the cohesional force between the particles is greater in the case of direct contact than when the contact takes place only through the solvation envelopes, then the forces necessary to cause equal deformation in the mass will depend on the existence and thickness of this envelope at the points of contact between the particles. These forces will be less in presence of structures caused by the elasticity of solvation envelopes (layers or liquid between the particles); they will increase in the case of coagulational structures, caused by the forces of molecular attraction at points covered by thinner aqueous coatings. These structures, according to Rebinder [6] have considerably greater limiting shear stress than the structures of the first type. Elastic, recoverable deformations of clay minerals, according to Denisov [14], appear as the result of changes in the thickness of the layer of bound water on the surfaces of the clay particles. Under the action of mechanical forces the thickness of this layer may decrease, as the result of partial displacement of water, at the points of contact of the particles during deformation. When the pressure decreases the water which was displaced returns again.

Thus, elastic deformations should be greatest in masses containing hydrate kaolin particles, and should decrease with decreasing thickness of the hydrate layer.

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Received February 23, 1953

EFFECT OF MOLECULAR INTERACTION ON THE LIGHT SCATTERING OF RUBBER SOLUTIONS

V. E. Gul and G. S. Klitenik

In the previous communications [1] it was shown that such important physical properties of rubbers as tensile strength, fatigue resistance, swelling, and others, are to a great extent determined by the nature and the intensity of the molecular interaction of the polymer.

An attempt is made in the present paper to examine the effect of molecular interaction in rubber solutions on the nature of molecular light scattering. Study of molecular light scattering provides very useful information on the structure of liquids, colloidal systems, and molecules, and has repeatedly been applied with success to the solution of problems of this type [2].

EXPERIMENTAL

The materials selected for study were solutions of natural smoked sheet rubber, not aged and subjected to thermal aging in an air thermostat for 18 days at 70°. At the same time investigations were made on solutions of butadiene-nitrile rubbers which differed in the content of nitrile groups in the copolymer molecule.

The solutions of natural rubber were prepared under such conditions that the action of oxygen was excluded. Toluene was used as the solvent. All the solvents used were dried over calcium chloride, twice distilled over metallic sodium, and twice filtered through a No. 4 glass filter. Before dissolving, the material was purified to remove impurities which are commonly present together with the rubber hydrocarbon in smoked sheet. The polymer solutions were repeatedly filtered through a No. 3 glass filter.

The butadiene-acrylonitrile copolymer solutions were prepared as follows. The polymer was first extracted with distilled water. Methyl ethyl ketone was used as the solvent The product was reprecipitated by the addition of definite amounts of methyl alcohol to the solutions. The solutions of butadiene-acrylonitrile copolymers were also prepared with strict exclusion of atmospheric oxidation, all the operations being carried out in an atmosphere of purified nitrogen.

The choice of methyl ethyl ketone as solvent was due to the fairly good solubility of the copolymers used in ketones, and the sufficiently great difference in the refractive indexes of the copolymer and solvent, which is necessary to attain the required accuracy in the measurements of the intensity of light scattering.

During the solution of the copolymers it was observed that in some cases solution was not complete. The solubility of the copolymer, and also the amount of non-solvent required to precipitate the copolymer from solution, depended on the nitrile group content in the copolymer.

To avoid inaccuracies in the determination of the percentage content of nitrile groups in the copolymers, the acrylonitrile content of the copolymers was determined (Table 1), both before and after dissolving. It was found that the nitrile group content was practically the same in the dissolved and the insoluble portions of the copolymer.

The optical scheme of the equipment used for measuring the intensity of light scattering by polymers is shown in Figure 1. Light from a mercury vapor lamp SVDSh-1000-3 passes through a light filter 2 with a maximum transmission of rays of wave length about 5460 A, then it passes through a condenser 3 into the nephelometer case 12. The main part of the light beam passes into the cell 5 which contains the solution studied. A small part of the light beam is reflected by the opaque glass 4, is weakened by the turbid object 6, and reaches the photometric head of a Pulfrich photometer. The light scattered by the solution from the cell 5 also enters the photometric head, where its intensity is compared with a standard. The remaining designations are seen in Figure 1, where 7 is the diaphragm; 8 is the objective; 9 and 10 are prisms; 11 is the eyepiece; 14 is the measuring dial.

The refractive indexes of solutions of different concentrations were measured with a Pulfrich refractometer.

TABLE 1

Acrylonitrile Content in the Dissolved Portion of the Copolymers

Polymer	Nitrogen content, %	Acrylonitrile content, %
N-6	–	6
N-18	4.8	18.4
N-28	7.4	28.5
N-36	9.5	35.1

Note. The following additions of methyl alcohol were required to precipitate from 500 ml solution: N-36 copolymer, 350-400 ml; N-28 copolymer, 250-270 ml; N-18, 150-170 ml.

The results of these measurements are shown in Figure 2 and Table 2.

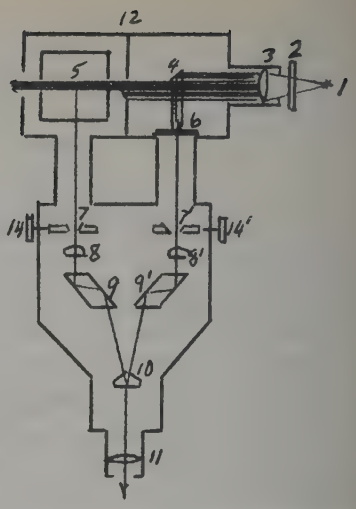

Fig. 1. Optical scheme of the nephelometer (explanation in text).

Turbidity measurements on the solvents used gave the following results: the turbidity of a mixture of toluene and 5% methyl alcohol was $2.74 \cdot 10^{-4}\ cm^{-1}$, and the turbidity of methyl ethyl ketone was $1.56 \cdot 10^{-4}\ cm^{-1}$. Figures 3 and 4 show the dependence of $H\frac{c}{\tau}$ on the solution concentrations, and also give the calculated values of the molecular weights of the high polymers.

In addition to investigations of solutions of substances which differ in their contents of groups of atoms active in the sense of molecular interaction in chain molecules, it was also of interest to study solutions which differed in the polarities of the solvents used. Such solutions may be prepared most simply by the use of binary solvents with different ratios of polar and nonpolar liquids. We determined turbidities of solutions of natural rubber in toluene and of butadiene-acrylonitrile copolymers in methyl ethyl ketone, containing different amounts of methyl alcohol. Figures 5 and 6 show graphically the dependence of the turbidity on the CH_3OH content.

TABLE 2

Refractive Indexes of Solutions of Different Concentrations

Polymer	Solvent	$H = \frac{32\pi^3 n_2^1}{3\lambda^4 N_A}\left(\frac{\partial n}{\partial c}\right)^2$
N-18	Methyl ethyl ketone	$17.90 \cdot 10^{-6}$
N-28	" " "	$9.80 \cdot 10^{-6}$
N-36	" " "	$7.19 \cdot 10^{-6}$
Natural rubber	Toluene + 5% methyl alcohol	$2.86 \cdot 10^{-6}$
Natural rubber after aging	Ditto	$2.63 \cdot 10^{-6}$

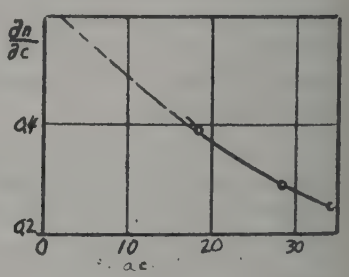

Fig. 2. Dependence of $\frac{\partial n}{\partial c}$ on the acrylonitrile content of copolymers.

A theoretical analysis of the results obtained is possible by the use of theories of molecular light scattering by high polymer solutions. Dogadkin, Soboleva, and Arkhangelskaya [3] experimentally proved the applicability of the relationship [4] to solutions of rubber:

$$H\frac{c}{\tau} = \frac{1}{M} + 2B_{\pi}c, \qquad (1)$$

where H is a constant determined refractometrically; τ is the turbidity produced by the dissolved polymer; M is the molecular weight of the polymer; B_{π} is a constant which depends on the solvent and the polymer; c is the concentration. Nevertheless, we considered it important to obtain confirmation of the validity of Equation (1) for the present case of light-scattering by natural rubber in a binary solvent. Data from the determination of the molecular weight of non-aged natural rubber by the osmotic method, M_{os} = 370,000, and viscosimetrically, M_{visc} = 380,000 were evidence of the low degree of polydispersity of this product [7]. In this case closeness between the values of the molecular weight determined by the osmotic method and from Equation (1) would support the validity both of Equation (1) itself, and of the assumptions on which its derivation is based.

Figure 7 shows results of the determination of the molecular weight of natural rubber by the osmotic method, from which it is seen that, for non-aged natural rubber with a low degree of polydispersity, the values of the molecular weights found by the osmotic method and by light scattering are very close to each other.

DISCUSSION

A theoretical examination of the molecular light scattering and osmotic pressure effects of solutions of high polymers leads to the conclusion that the angular coefficients of the concentration lines $H\frac{c}{\tau} - c$ and $\left(\frac{\pi}{c} - Kc\right) - c$ depend on the intensity and nature of the forces of molecular interaction of the mixed components, and also on other factors.

Thus, for example, the angular coefficient of the concentration graph $\left(\frac{\pi}{c} - Kc^2\right) - c$, which we will denote by B_π, is related to the value

$$\mu_1 = \frac{\beta}{RT} V_1 + \frac{1}{z}\left(1 + \frac{4}{3}\frac{v_2}{z}\right)\left(1 - \frac{1}{x}\right) \qquad (2)$$

in the following way:

$$B_\pi = A\left(\frac{1}{2} - \mu_1\right) \qquad (3)$$

where A is a constant. Equation (2) shows that μ_1 depends on v_2, the molecular fraction of the polymer in solution, on β, which is a measure of the molecular interaction of the components, on z, which is the coordination number of the quasicrystalline lattice, and on x, the degree of polymerization of the polymer.

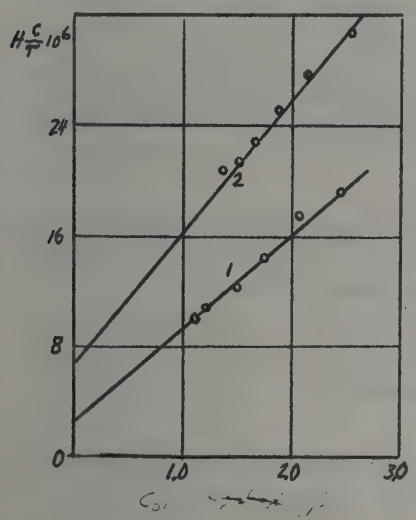

Fig. 3. Dependence of $H\frac{c}{\tau}$ on concentration for natural rubbers: 1 - before aging; M = 370,000; $B_\tau = 6.7 \cdot 10^{-3}$. 2 - after aging; M = 149,000; $B_\tau = 9.5 \cdot 10^{-3}$.

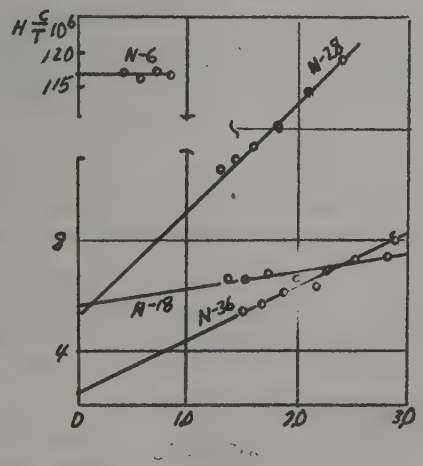

Fig. 4. Dependence of $H\frac{c}{\tau}$ on concentration for copolymers N-28 (M = 192,000; $B_\tau = 3.86 \cdot 10^{-3}$); N-36 (M = 399,000; $B_\tau = 1.94 \cdot 10^{-3}$); N-18 (M = 180,000; $B_\tau = 0.67 \cdot 10^{-3}$) and N-6 (M = 8600; $B_\tau = 0$).

By means of Equations (2) and (3) and with the use of the molecular weight values of the rubber samples it can be easily shown that, for the samples of oxidized and unoxidized rubber in question, changes of B_π due to different values of v_2 and x are so slight that they may be neglected. The differences in the slopes of the concentration graphs are therefore due mainly to variations of the energy factor β, which is associated with accumulation of polar oxygen-containing groups of atoms in the molecule.

It is worthy of notice that the angular coefficient of the $H\frac{c}{\tau} - c$ curve, which will be denoted by B_τ, has a greater value than the theoretically expected. According to the theoretical views developed by Debye and Einstein, $B_\tau = 2B_\pi$, which is not always true for solutions of rubber. However, apparently the nature of B_τ and B_π which determines the increase or decrease in the values of $H\frac{c}{\tau}$ and $\frac{\pi}{c} - Kc^2$, remains the same as the concentration of polymer in the solution increases.

The increase of $\frac{\pi}{c}$ with increasing concentration is evidence of the increasing tendency of the components

to mixing as the number of polymer particles in the solution increases. The value of $\frac{\pi}{c}$ for the specific osmotic pressure per unit concentration describes the tendency of the solvent molecules to mix with the polymer molecules. This tendency, which depends on both entropy and energy factors, may decrease with increase in the concentration of polymer particles in the solution, or, conversely, may increase, depending on the nature of the variations of the entropy and energy factors with concentration.

However, if the fact that in real systems the relationship $B_\tau = 2B_\pi$ is not always true is not taken into account, conclusions may be drawn which are not strictly accurate. For example, Bechtold [5]

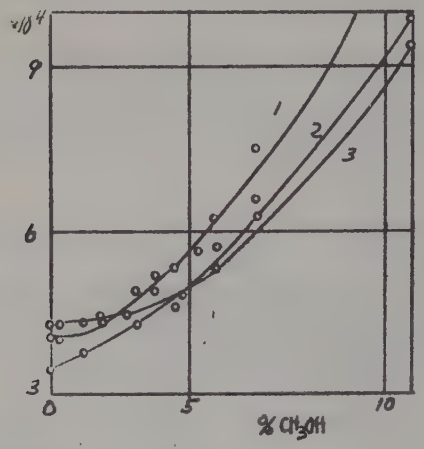

Fig. 5. Dependence of the turbidity of solutions of natural rubber on the volume content of methyl alcohol: 1 — rubber before aging; 2 — after 9 days, and 3 — after 18 days aging.

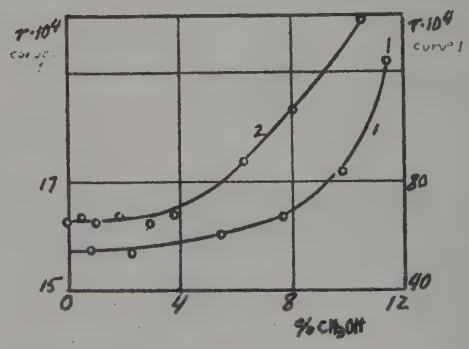

Fig. 6. Dependence of turbidity on content of methyl alcohol: 1 — for solution of N-28; 2 — for solution of N-18.

examined an interesting case of simplified procedures in connection with characterization of polymers by their number-average M_n and weight-average M_w molecular weights. His proposed relationship between the weight-average and the number-average molecular weights M_x is based on the assumption that $B_\tau = 2B_\pi$.

Experimental verification of his proposed method showed that the value M_x characterizes not so much and not only the relationship of M_n and M_w, but rather the absolute values of the molecular weights M_n and M_w. A more exact characterization in this sense was provided by the values of $K_w = M_w/M_x$ and $K_n = M_n/M_x$, which are linearly related to the value of $K_p = M_w/M_n$.

However, the use of the value of M_x for calculations of this type is valid only when $B_\tau = 2B_\pi$. As this is not always true for rubber solutions, it is necessary to introduce certain corrections. If, instead of the previously assumed relationship $B_\tau = 2B_\pi$, we take those found experimentally: $B_\tau/B_\pi = K_1 = 10.56$, and $B_\tau/B_\pi = K_2 = 13.59$ for aged rubber, then the value of M_x calculated from the values of M_w and M_n is in good agreement with the value calculated from the values of τ and π. Figure 8 shows the dependence of K_w and K_n on K_p, based on experimental data for different natural rubbers.

In view of the above considerations, the equation (3) proposed by Bechtold:

$$\frac{1}{M_n} = \frac{\pi}{RTc} - \frac{Hc}{2\tau} + \frac{1}{M_w}$$

should be replaced by

$$\frac{1}{M_n} = \frac{\pi}{RTc} - \frac{Hc}{K\tau} + \frac{1}{KM_w}, \qquad (4)$$

where K is determined experimentally for any given polymer-solvent pair. With the use of equation (4), it is possible, with a knowledge either of M_w or of M_n to determine the other, when only one value for the turbidity or osmotic pressure of the solution is available. This is particularly convenient when it is not possible to determine M_w or M_n with sufficient accuracy for a given polymer (if the polymer molecules are very small or very large).

Examination of the results shown in Figure 4 clearly shows that the angular coefficients of the concentration graphs do not change regularly with increase of the nitrile group content in butadiene-acrylonitrile copolymers. Our calculations showed that the effect of the molecular weight difference on the slope of the

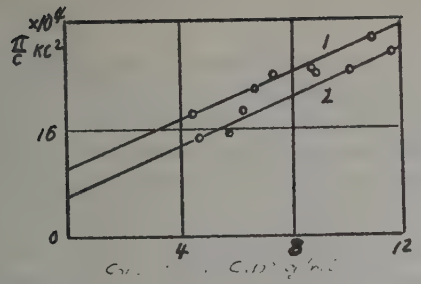

Fig. 7. Results of molecular weight determinations for natural rubber: 1 — after 18 days aging ($M = 233,000$; $B_\pi = 0.70 \cdot 10^{-3}$); 2 — before aging ($M = 366,000$; $B_\pi = 0.635 \cdot 10^{-3}$)

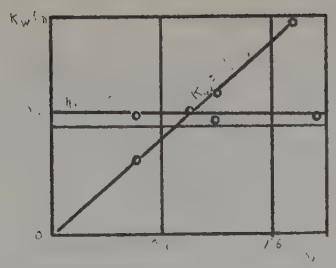

Fig. 8. Dependence of $K_w = \frac{M_w}{M_x}$ and $K_n = \frac{M_n}{M_x}$ on $K_p = \frac{M_w}{M_n}$

straight lines does not exceed 0.6%.

Figure 9 shows the manner in which the angular coefficients of the linear graphs $H\frac{c}{\tau} - c$ for solutions of butadiene-acrylonitrile copolymers vary with the nitrile group content. The lack of regularity of the variation of the angular coefficients of the lines follows from equation (2). As was already shown earlier, changes in B_π are produced mainly by changes in the nature of the molecular interaction. In accordance with equation (3) B_π changes with changes in μ_1 in such a way that it may theoretically assume a value from 0.5 Å when $\mu_1 = 0$, to relatively large negative numbers. In the experimental results presented here B_τ, and consequently B_π, were always positive.

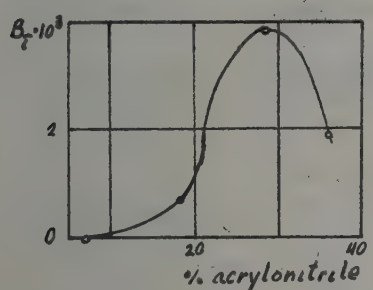

Fig. 9. Dependence of the angular coefficient of $H\frac{c}{\tau} - c$ on the acrylonitrile content in copolymer solutions.

The value $B_\pi = 0.5$ Å is obtained only when $\mu_1 = 0$; i.e.,

$$\beta = -\frac{RT}{V_1 z}\left(1 + \frac{4}{3}\frac{v_2}{z}\right)\left(1 - \frac{1}{x}\right) \qquad (5)$$

which is impossible, as β is the square of a finite value, and is consequently always positive.

The values of B_π and B_τ are equal to zero when $\mu = 0.5$. In this case β should have a quite definite value:

$$\beta = \frac{0.5\,RT}{V_1} - \frac{RT}{V_1 z}\left(1 + \frac{4}{3}\frac{v_2}{z}\right)\left(1 - \frac{1}{x}\right) \qquad (6)$$

This value of β is attained both for a positive and a negative difference $\sqrt{\frac{E_1}{V_1}} - \sqrt{\frac{E_2}{V_2}}$.

A necessary condition is that:

$$\sqrt{\frac{E_2}{V_2}} = \sqrt{\frac{E_1}{V_1}} \pm \sqrt{\frac{1.5RT}{V_1} - \frac{RT}{V_1 z}\left(1 + \frac{4}{3}\frac{v_2}{z}\right)\left(1 - \frac{1}{x}\right)} \qquad (7)$$

In the case in question an accumulation of polar groups should lead to a steady variation of the molecular interaction in the direction of an increase in the intensity of orientational and inductional interaction. The value of E_1/V_1 then remains constant, while E_2/V_2 varies. When E_2/V_2 begins to satisfy the condition given by equation (7), $B_\pi = B_\tau = 0$. Also, according to (7), this may occur for two values of E_2/V_2. The curve in Figure 9 clearly shows the tendency of B_τ to assume a value equal to zero at a further increase in the polar group concentration. Analogously with the above, when E_2/V_2 = constant, by suitable variation of the solvent, it is possible to obtain a curve analogous to that shown in Figure 9. From a knowledge of the value of E_1/V_1, for which $B_\tau = 0$, it is possible to determine the value of E_2/V_2.

Thus, the determination of $B_T = f(E_1/V_1)$ where E_1 and V_1 are the specific cohesional energy and the molecular volume of the solvent respectively) is a convenient method for the determination of the specific cohesional energy of a high polymer.

Determination of the effect of the percentage content of methyl alcohol on the turbidity of solutions of natural rubber in toluene showed that the turbidity of the system did not vary regularly with addition of the polar solvent. This effect was already described previously by Dogadkin and Soboleva [6]. In our view this effect is due to the fact that initially additions of CH_3OH decrease the difference in the nature of the molecular interaction in rubber and in the binary solvent. Further addition of CH_3OH is accompanied by an increase in the difference of the intensity and the nature of the molecular interaction of the rubber and the solvent.

Accordingly, a decrease in the heterogeneity of the field of force of molecular interaction is accompanied by a decrease in the intensity of fluctuations and consequently by a decrease in the intensity of light scattering. Further addition of CH_3OH, which again increases the heterogeneity of the field of force of molecular interaction, again results in an increase in the turbidity of the solution.

An increase in the polarity of the chain molecules of the high polymer is accompanied by an increase in the amount of polar solvent which must be added to produce a minimum value of the turbidity of the solution. This effect is somewhat distorted by the change of turbidity which occurs as the result of an increase in the difference between the coefficients of refraction of the polymer and the solvent.

SUMMARY

1. A study was made of the molecular light scattering of solutions of rubber, which differed in varying polarities of the dissolved high polymers and of the solvent mixtures used.

2. The dependence of the angular coefficient of the light scattering concentration curves on the molecular interaction and other factors is examined theoretically.

3. A relationship is proposed by which it is possible to simplify the procedure of the experimental characterization of polymers by the number-average and weight-average molecular weights.

4. A method is proposed for determination of the specific cohesional energy of high polymers from light scattering data for their solutions.

The authors express their gratitude to L. G. Soboleva for the discussion of the results obtained in the present investigation, and for her valuable comments.

Moscow Institute of Fine Chemical Technology Received January 6, 1954.

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THE STRUCTURE OF GELS

V. PREPARATION OF GLOBULAR CASEIN

P. I. Zubov, Z. N. Zhurkina, and V. A. Kargin

In our studies [1], it was shown that the mechanism of formation of protein gels consists of the formation of local bonds between the more active groups which compose the linear protein molecule. The network gel structure formed as the result of such interaction shows various relaxational properties according to the polymer concentration. In dilute gels, in which interaction between the chains is weak, only small relaxation periods are present. In concentrated gels, as the result of strong interaction between the chains, the situation changes in favor of an increase in the selection of relaxation periods. As regards the nature of the local bonds between the chains, this remains the same both in dilute and in concentrated gels.

The formation of a gel is always associated with a definite concentration of the gel-forming substance in solution. In presence of a large amount of solvent, intermolecular local bonds cannot be formed by the interaction of active groups which are contained in the chain molecules. In such solutions the formation of a continuous network structure in the gel is excluded. If it is taken into account that, as the result of its flexibility and thermal motion, the large polymer molecule continuously changes its shape, then it is possible for active groups to come into proximity and for bonds to be formed between them within the limits of one or a few molecules.

We established [2] that by removal (evaporation) of water from a dilute solution at low temperature, it is possible to obtain gelatin which shows the properties of a globular protein (solubility in water at room temperature). An important defect of globular gelatin is its insufficient stability to the slightest fluctuations of temperature, which is due to the weakness of the local bonds.

The present study is devoted to the preparation of the globular form of casein from normal casein, the local bonds of which are so strong that it does not dissolve even in boiling water. In the preparation of globular casein, a weighed sample of air-dry casein, after preliminary swelling at room temperature, was dissolved in 0.1 N $Ba(OH)_2$ at approximately 50°, the solution was then diluted with redistilled water to a 0.2% concentration, and held at this temperature for 15 minutes. The solution was then cooled to 0-5°, and an equivalent amount [with respect to the $Ba(OH)_2$] of 0.1 N H_2SO_4 was added, and the $BaSO_4$ formed was separated from the solution with a centrifuge operating at 12,000-14,000 rev/min. The solution was then evaporated in a vacuum to remove water completely, as in the production of globular gelatin. The dry casein was obtained in the form of a hard, glassy mass, which dissolves in water to form a weakly opalescent solution.

This experiment was reproduced repeatedly later, and in all cases casein soluble in cold water (12-15°) was obtained. It is only necessary to observe strict equivalence of the baryta and sulfuric acid.

From the results of these experiments it was possible to conclude that we did in fact obtain a new variety of casein (the globular form). The solubility of globular casein, in our view, is due to the fact that the major part of the polar groups of the molecules is mutually saturated as the result of intramolecular interaction, that is, in the process of formation of globular structures.

Evidence of the weak interaction between the particles of anhydrous globular casein and of the loss of the high elasticity properties characteristic of linear chains, is provided by our data on the mechanical properties of films prepared from aqueous glycerin solutions of the casein.

Table 1 shows comparative data on the mechanical strength of films prepared from aqueous solutions of globular and normal casein, in presence of 25% glycerin.* The tests were made on a Schopper type tensile

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*When normal casein was dissolved, several drops of 25% ammonia solutions were added to the mixture and this was then heated to 40-50°.

testing apparatus [3]. The test specimens were prepared from films 0.1-0.15 mm thick.

TABLE 1

Results of Mechanical Tests on Films Prepared from Normal and Globular Casein

Storage time of film (in days)	Type of casein	Tensile strength in kg/cm²	Mean elongation in %
15	Normal	210	107
45	"	284	65
11	Globular	184	4
38	"	112	2

Note. The tensile strength was calculated for the cross-sectional area at break.

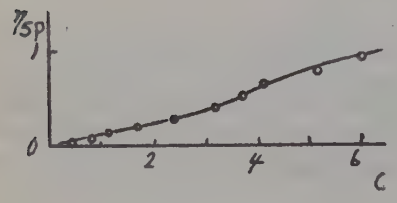

Fig. 1. Dependence of the viscosity of solutions of globular casein on dilution.

The values shown for the tensile strength represent the mean of 5-7 determinations, which showed deviations of 20-50%. Nevertheless, these results clearly show the difference between films of normal and globular casein. Films from normal casein have high elasticity and a greater value of the modulus, while films of globular casein have a hard (glassy) structure and a lower elasticity modulus. There is no doubt that this is due to a different distribution of bonds formed between the polar groups of the protein (intra- and intermolecular bonds).

Evidence of the weak interaction between the particles in solutions of globular casein is also provided by the data shown in Figure 1 on the viscosities of its solutions. The viscosity measurements were carried out with an Ostwald viscosimeter.

It is seen from the data of Figure 1 that the specific viscosity of globular casein up to 6% concentration is comparable with the viscosity of hydrophobic rather than hydrophilic colloidal solutions. All this is evidence of the presence of firm intramolecular bonds localized within the limits of one or several molecules.

Since there is no doubt concerning the presence of intramolecular bonds in globular proteins, it was of interest to compare the sorptional capacity of this type of casein with the sorptional capacity of normal casein. Table 2 shows data on the sorption and desorption of both types of casein. The experiments were made with a MacBain balance [4].

It may be seen from the results given in Table 2 that globular and normal casein are indistinguishable in their sorption and desorption of water. Consequently, the formation of globular structures of casein is not associated with changes of activity with respect to water. This means that the nature of interaction between polar groups is the same in both forms, and only the distribution of the same amounts of bonds varies.

TABLE 2

Sorption and Desorption of Water Vapor by Globular and Normal Casein

Sorption				Desorption			
Time (in hours)	Relative humidity (in %)	% Increase in weight		Time (in hours)	Relative humidity (in %)	% Increase in weight	
		Globular casein	Normal casein			Globular casein	Normal casein
48	27	7.3	7.1	48	63.5	14.6	14.7
24	58	11.9	12.5	48	15.0	5.8	6.0
48	72	16.9	17.4	96	0.0	0.4	0.0
48	86	24.3	23.9				

We established also that globular casein, like any globular protein, is capable of denaturation. We found on heating a solution of globular casein in a sealed ampoule on an oil bath that the solution begins to go turbid at 90-100°. Further increase of temperature to 120° produces a division of the system into two phases: a fibrous precipitate and a clear solution.

It is particularly interesting that denaturation of the casein (formation of a precipitate) commences on the addition to the solution of small amounts of alkali, which, as is known, dissolves ordinary casein. The precipitate formed dissolves in excess alkali, which is evidence that after the rupture of intramolecular local bonds the globular form of casein disappears, and normal fibrous casein is formed. Denaturation of globular casein takes place also in the presence of strong electrolytes (common salt, ammonium nitrate, etc.). Therefore, denaturation of proteins, which in the present case is facilitated by the addition of a small amount of alkali, is principally a process of redistribution of local bonds.

Denaturation of the casein does not occur on the addition of alcohols, urea, and also of acid to the solution. This indicates the presence of an excess of acid groups contained in globular casein. To verify this supposition, we made a detailed study of the electrochemical properties of globular casein. These experiments are also interesting because up to the present time, because of its insolubility in water, casein has been studied electrochemically mainly only in the alkaline region.

The solubility of our globular casein in water makes it possible to study its properties both in the alkaline and the acid region. It may be supposed that the solubility of globular casein in water is due to a shift of the acid-alkaline equilibrium as a result of the nonequivalent hydrolytic sorption of Ba^{2+} and SO_4^{2-} at the polar groups of casein. This assumption is possible, as $BaSO_4$ is soluble, although slightly, in water. Therefore, before experiments to study the electrochemical properties of casein from all aspects, experiments were carried out in order to establish the presence or absence of hydrolytic sorption.

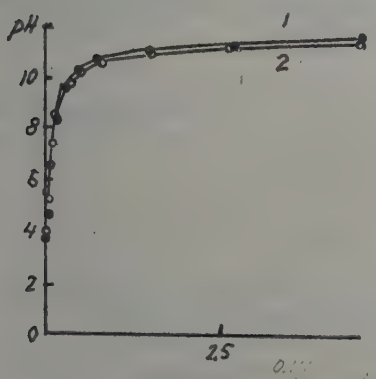

Fig. 2. Titration of filtrates after shaking casein with redistilled water and with a mixture of barium hydroxide and sulfuric acid.

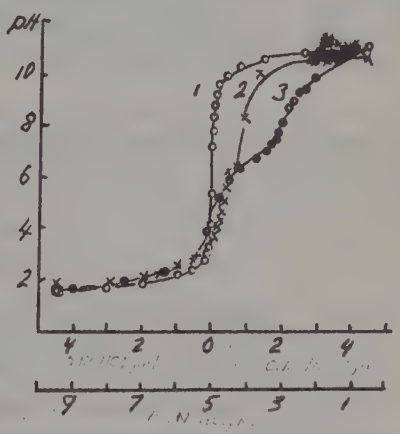

Fig. 3. Titration of 1 – redistilled water, and 0.42% solutions of 2 – globular, and 3 – normal casein.

A finely divided sample of normal casein was divided into two portions. One portion was mixed with water, and the other with an equivalent mixture of 0.1 N solutions of baryta and sulfuric acid. Both suspensions were then shaken for two hours at 40°. The precipitates were then separated off in the centrifuge, and the solutions titrated with the aid of the glass electrode, hydrogen being passed continuously through the solution being titrated. The titration was with 0.1 N alkali solution.

Figure 2 shows that practically no shift of the acid-base equilibrium occurs; the pH of the solution from the mixture of casein and baryta differs from that of the aqueous extract only by 0.2 of a pH unit. This variation, of course, cannot affect the solubility of casein, as it does not exceed the limits of the pH of pure water. From this it may be concluded that the solubility of globular casein is not related to hydrolytic sorption.

In conclusion, we present our data on the acid-alkali titration of globular casein over the entire pH range. It can be seen from Figure 3 that globular casein shows the behavior of a normal protein, containing acid and alkaline groups. Comparison of data on the titration of normal casein, shown in curve 2 of Figure 3, shows that globular casein contains a smaller amount of alkaline groups; this indicates the disappearance of part of the alkaline groups during the formation of globular casein. For this reason the isoelectric point of globular casein lies below that of normal casein.

At a high content of alkali in the solution the distinction between globular and normal casein disappears, which is quite explicable, as in these conditions, as was seen in the data on denaturation, all the intramolecular bonds in globular casein are broken, and therefore it practically does not differ from normal casein.

It also follows from all these results that the formation and destruction of globular forms of casein is associated with the formation and rupture of intramolecular local bonds only. No formation of new polypeptide linkages takes place in the transition of casein into the globular form.

SUMMARY

1. Globular casein has been obtained, which has a more stable structure than globular gelatin.

2. Globular casein dissolves in cold water to give solutions the viscosity of which varies according to a linear law over a wide range of concentrations.

3. Films of globular casein differ from films of normal casein by a lower value of the elasticity modulus and the absence of high elastic properties.

4. Globular casein, like natural globular proteins, is capable of denaturation in definite conditions.

5. The sorptional capacity of globular casein is the same as that of fibrous casein, which is evidence of the same nature of the local bonds in both the forms of casein. Globulization and denaturation are due only to a redistribution of the same number of bonds.

6. Electrochemical measurements show that the number of alkaline groups is smaller in globular than in alkaline casein. After denaturation of globular casein this difference vanishes.

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Received January 13, 1954.

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BEHAVIOR OF A TWO-COMPONENT SUSPENDED LAYER

A. M. Koganovsky and V. G. Petrenko

The conditions of formation and stability for a suspended layer of a solid phase dispersed in a stream are more or less clarified only for the relatively simple case of a layer of homogeneous granular material. For more complex systems, forming a suspended layer from a mixture of two or more dispersed components, the particles of which interact as the result of cohesion, the applicability of the relationships derived for layers of homogeneous free-flowing substances has not been clarified.

This refers in particular to systems one of the components of which is a colloid of the type of aluminum hydroxide or iron hydroxide flakes, as their suspensions generally readily form fairly stable supermicellar thixotropic structures and readily change the degree of dispersion of the secondary particles. At the same time, suspended layers of flakes of these hydroxides or of their mixtures with powders are widely used in the solution of a number of technical problems, in particular in improving the quality of potable and industrial waters.

We observed that mixing of flakes in a conical diffuser took place despite the very low value of the Reynolds number for the stream of liquid passing through the suspended layer ($Re = \frac{dw\gamma_c}{\mu g} \leqslant 0.3$). As far as can be judged from the literature data, turbulent flow of a liquid passing through a suspended layer commences at $Re \geqslant 7$. Comparison of our data with this critical value of the Reynolds number gives rise to the supposition that a turbulence in the suspended layer is also possible even under laminar flow conditions in the liquid passing through such a layer.

Smirnov and Li De En [1] proposed the following criterial equation to describe a suspended layer of a free-flowing substance in turbulent flow:

$$Eu = 8.58f \cdot Re^{-2.2} \cdot Ar\Gamma_1^{0.5} \cdot \Gamma_2^{1/3} \cdot \Gamma_3^{1/3}, \qquad (1)$$

where Eu is the Euler criterion which characterizes the resistance of the layer; f is the shape factor of the particles, equal to the ratio of the surface of a sphere to the surface of a particle of equal volume; Ar is the Archimedes criterion; Γ_1, Γ_2 and Γ_3 are the criteria of geometrical resemblance, respectively equal to d/D, h_0/D and h/D (d is the determining size of the particles; D is the diameter of the apparatus in which the suspended layer is produced; h_0 is the height of the precipitate in the apparatus in a stationary medium, and h is the height of the suspended layer in the stream).

Equation (1) was verified by the authors on extensive experimental material, and apparently gives quite satisfactory agreement between the calculated and experimental values of Eu. As was to be expected, equation (1) was most accurate in the range of $Re \geqslant 7$. The small amount of data obtained by Smirnov and Li De En in the study of a suspended layer of spheres in laminar flow regime shows that the essential form of the law is retained, but the experimental results always differ somewhat from the calculated, in the same direction. The authors of the equation, therefore, assumed that values of the constant and of the exponents of the criteria must be changed in the equation for conditions of laminar flow.

An attempt to examine our experimental data with the use of equation (1) showed that this equation is also quite satisfactory for the description of suspended layers of flakes of aluminum and iron hydroxide, and coal and chalk powders at $Re \leqslant 0.3$; i.e., in the laminar region of flow of the liquid through the layer. The size of the suspended particles was approximately 0.1 mm.

As can be seen from Figure 1, the experimental data for a suspended layer of aluminum hydroxide fit well into equation (1) under the condition that the constant has a value of about 3.26 instead of 8.58 (or the form factor a value of 0.38) and all the values of the exponents of the criteria are retained. The value f = 0.38 indicates an extended shape of the aluminum hydroxide particles, which is in agreement with known data on this subject. At flow rates below 1-0.8 mm/sec, the constant in equation (1) begins to increase. Since in this region ($Re \sim 0.1$) there should be no sharp change in the flow regime, which was laminar previously also, it should be assumed that

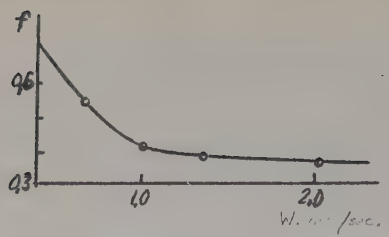

Fig. 1. Dependence of the shape factor, f, of suspended particles of aluminum hydroxide on the rate of flow of the stream, w, entering the layer.

the increase in the constant is due to an increase in the disordered aggregation of the particles in a very slow stream, and depends on the increase of the shape factor. Indeed, disordered aggregation should lead to a decrease in the ratio of the axes of the secondary particles, so that in the limit almost spherical lumps of flakes may be formed and the value of f reaches unity.

Our results obtained in the application of equation (1) to a suspended layer of two component mixtures present a fairly significant interest. On the basis of these results it was possible to evaluate the change in the shape factor of the secondary particles formed as a result of aggregation in the stream, in relation to the rate of motion and of the ratio of the components in the mixture. We have already indicated that the shape factor of particles suspended in a stream makes it possible to evaluate to a certain extent the orientation of the particles on cohesion, as a result of the fact that the hydroxide particles have an elongated or flat form.

To determine the shape factor it is necessary to compare the values of the Euler criterion determined direct from the ratio and calculated from the Smirnov and li De En equation on the assumption that f = 1 (that is, on the assumption that the particles are strictly spherical)

$$Eu = \frac{\Delta p g}{\gamma_c w^2},$$

where Δp is the pressure loss in the layer in kg/m^2; g is the gravitational constant in m/sec^2; γ_c is the density of the medium in kg/m^3; w is the rate of flow of the liquid entering the stream in m/sec, when

$$f = \frac{Eu_{actual}}{Eu_{Smirnov}} \qquad (2)$$

However, for the calculation of the Euler criterion from equation (1), it is necessary to know a number of values, most of which are determined by the conditions of formation of the suspended layer: the rate of flow w, the density γ_c and the viscosity μ of the dispersion medium, the diameter D of the apparatus in which the suspended layer is produced, the height h of the suspended layer at a given flow rate, and the height of the precipitate h_0 in a stationary dispersion medium. It is necessary to determine separately the density γ_s of the substance forming the dispersed phase of the suspended layer, and the diameter d of the suspended particles.

While the first of these values can be determined experimentally with sufficient accuracy even for flakes of aluminum and iron hydroxides, the degree of dispersion of particles of these substances can be determined approximately only, as any action on the secondary particles of the hydroxide coagulum changes its degree of dispersion sharply as the result of aggregation and disaggregation processes. For this reason it is not possible to apply either sedimentometry (as aggregation of particles will take place during their settling in a stationary medium) or ultramicroscopic counting for the determination of the degree of dispersion. As in our experiments the suspended layer was obtained in a conical diffuser of the type of a Teterkin clarifier [2], it proved possible to determine approximately the dimensions of the suspended substances with the use of the Schöne formula.

$$d = 0.0518 \frac{w_s^{7/11}}{\gamma_s - 1}$$

where w_s is the rate of flow of the stream leaving the layer; γ_s is the density of the dispersed substance.

It is evident that the Schöne formula, applied to the conditions of a suspended layer in a conical diffuser, only permits an evaluation of the size of the particles in immediate proximity to the upper surface of the layer. Therefore, in a consolidated suspension which a suspended layer is, the ability of the particles to cohere in flow should affect the experimental results in the sense that the particle size found will increase somewhat with increasing flow rate in restricted limits (in the cohesional region). Finally, in the case of powders, the density of which is sufficient for the larger particles to be deposited at low flow rates, an increase of the rate should also lead to a certain increase of the size found due to the larger particles which are carried into the upper portion of the suspended layer at the new flow rate. Nevertheless, the order of sizes determined by the Schöne formula should agree in the case of powders with the order of sizes as determined by sieve analysis.

TABLE 1

Results of Sieve Analysis of Coal Powder, and Particle Sizes by the Schöne Formula

(Diameter of sieve holes 0.088 mm)

Particle size by Schöne formula (in mm)	Rate of flow in mm/sec	
	On entering the layer	On leaving the layer
0.0661	0.68	0.64
0.0969	1.36	1.17
0.1193	2.04	1.62

The agreement of particle sizes determined by sieve analysis and by the Schöne formula, in which the value of the flow rate at the upper surface of the layer was substituted, was verified for a fraction of activated birchwood charcoal which passed a mesh with 4900 holes/cm^2 (d = 0.088 mm). As can be seen from the results shown in Table 1, the agreement can be considered satisfactory.

We give below the results of a study of the behavior of mixtures of aluminum hydroxide flakes with powdered activated charcoal and chalk powder suspended in a stream, and also that of mixtures of iron hydroxide flakes with powdered activated charcoal. The powder fractions used were those passing through a sieve with 4900 holes/cm^2. In an ascending stream of water, these systems formed a practically homogeneous suspended layer because of the adhesion of the powder particles to the flakes. Even after prolonged existence of such a two component suspended layer, no significant separation of one of the components was observed, and in this respect the layer was quite similar to an ordinary one component suspended layer.

The scheme of the apparatus with which the experiments were carried out did not differ from that described in the preceding paper [3]. After the suspended layer had been kept for an hour at a constant volume rate of flow of the stream, its height reached a value which was practically constant for the given experiment as equilibrium became established between the aggregation and disaggregation processes in the suspension. The height of the layer was measured to an accuracy of 5 mm at the ninetieth minute of operation of the diffuser. A greater accuracy of measurement was unattainable, as the surface of the suspended layer fluctuated all the time, resembling the boiling surface of a viscous liquid, in particular when the flow rate of the water was high. The sedimentational volume and height of the precipitates in the clarifier diffuser were determined in special experiments.

Table 2 shows our results for a suspended layer of mixtures of activated charcoal with aluminum hydroxide at rates of flow of 0.68, 1.36, and 2.04 mm/sec of the stream entering the layer, but with a constant amount, m, equal to 10 g of the mixture, of the suspended substance. It was not possible to establish a simple relationship between the flow rate of the stream leaving the layer in the conical diffuser, and its height. For this reason all the calculations (with the exception of the calculation of the degree of dispersion) were made using the rate of the stream feeding the layer.

TABLE 2

Dependence of the Shape Factor f of the Particles in a Suspended Layer of Mixtures of Aluminum Hydroxide with Activated Charcoal on the Ratio of the Components and the Rate of Flow

(m = 10 g; D = 0.082 m at the entry into the layer)

% $Al(OH)_3$	% Charcoal	w = 0.68 mm/sec Eu = 165.18			w = 1.36 mm/sec Eu = 41.29			w = 2.04 mm/sec Eu = 18.35		
		d $m \cdot 10^{-6}$	Re	f	d $m \cdot 10^{-6}$	Re	f	d $m \cdot 10^{-6}$	Re	f
100	0	115	0.0693	0.54	163	0.1964	0.38	175	0.3163	0.36
80	20	63.5	0.0382	0.66	88.2	0.1063	0.48	100.5	0.1816	0.42
60	40	47	0.0283	0.67	66.0	0.0795	0.51	73.3	0.1325	0.43
40	60	41.5	0.0250	0.73	63.2	0.0761	0.49	63.2	0.1142	0.43
20	80	42.4	0.0255	0.67	57.6	0.0693	0.48	64.5	0.1166	0.42
5	95	52.7	0.0317	0.80	71.6	0.0863	0.54	80.2	0.1449	0.46
0	100	88	0.0526	1 *	96.9	0.1167	0.95	—	—	0.95

* In view of the insignificant height of a suspended layer of pure charcoal and an insufficiently distinct separation boundary due to the polydispersity of the suspension, the shape factor could only be determined very approximately.

Tables 3 and 4 show analogous data which show the relationship between the shape of the particles on the ratio of the components and the rate of flow of the stream in suspended layers of mixtures of aluminum hydroxide with chalk and of iron hydroxide with activated charcoal.

TABLE 3

Dependence of the Shape Factor f of the Particles in a Suspended Layer of Mixtures of Aluminum Hydroxide with Chalk on the Ratio of the Components and the Rate of Flow.

(m = 10 g; D = 0.082 m at the entry into the layer)

% $Al(OH)_3$	% Chalk	w = 1.02 mm/sec Eu = 73.4			w = 2.04 mm/sec Eu = 18.3		
		d $m \cdot 10^{-6}$	Re	f	d $m \cdot 10^{-6}$	Re	f
100	0	150	0.1355	0.41	175	0.3163	0.36
80	20	39.5	0.0357	0.62	53.7	0.0970	0.39
60	40	25.8	0.0233	0.62	34.5	0.0623	0.52
40	60	—	—	—	29.0	0.0524	0.52
20	80	19.9	0.0180	0.78	27.8	0.0502	0.53

TABLE 4

Dependence of the Shape Factor f of the Particles in a Suspended Layer of Mixtures of Iron Hydroxide with Activated Charcoal on the Ratio of the Components and the Rate of Flow

(m = 10 g; D = 0.082 m at the entry into the layer)

% $Fe(OH)_3$	% Char-coal	w = 0.68 mm/sec Eu = 165.2			w = 2.04 mm/sec Eu = 18.3		
		d $m \cdot 10^{-6}$	Re	f	d $m \cdot 10^{-6}$	Re	f
100	0	149.1	0.0898	0.42	189.0	0.3416	0.28
80	20	106.0	0.0638	0.46	131.9	0.2384	0.33
60	40	78.2	0.0471	0.56	108.4	0.1959	0.35
40	60	68.5	0.0413	0.58	101.0	0.1959	0.35
20	80	63.2	0.0381	0.71	100.0	0.1807	0.38
5	95	62.9	0.0379	0.95	113.9	0.2058	0.43
0	100	88.0	0.0526	1	119.0	—	0.95

Comparison of the values of the shape factor for suspended particles of aluminum hydroxide at different flow rates (Figure 1) shows that f does not vary significantly at rates above 1-1.1 mm/sec. In the conditions of the experiments these rates correspond to a value of Re $\simeq$ 0.1. At a flow rate of about 1 mm/sec, the shape factor reaches a definite minimum value. Therefore, it does in fact show variations of the shape of the particles under the influence of their aggregation and orientation in a stream. As can be seen from the data in the tables, variations of the composition of the mixture in wide limits (from 20-90% of the powder component) result in practically no change in the shape factor of the suspended particles.

The values of f obtained for a suspended layer of pure hydroxides of aluminum or iron are a little lower than the values of f for mixtures, but the shape factor increases even on a very slight addition of the powdered component. This increase of the shape factor, which indicates a decrease of the ratio of the particle axes, is apparently due to the densification of the secondary particles under the action of cohesion. This densification of the particles in mixtures probably also causes the decrease in their dimensions in comparison with the secondary particles of the components.

A suspended layer of powdered charcoal without admixtures of hydroxide has a shape factor which approximates to unity, which indicates an irregular shape of these particles with approximately equal values of the axes of symmetry. The values of f found for suspended layers of hydroxides and their mixtures with powders indicate an elongated or flattened shape of the particles, as the surface area of such particles considerably exceeds the surface area of spherical particles with an equal volume (f = 0.3-0.5). A sharp transition from the elongated particles in a suspended layer of mixtures to the irregular particles of a suspended layer of charcoal takes place only when the hydroxide content in the mixture is decreased to 5%. Consequently, adhesion processes in a suspended layer of a mixture of hydroxide and powder take place not in a chaotic but an oriented manner.

It is interesting that with a constant value of the Euler criterion the shape factor in mixtures does not vary, despite sharp changes in all the parameters which characterize the suspended layer (ratio of the components, dimensions of the particles, height of the layer and of the precipitate, density of the mixtures, and the rate of flow of the stream on leaving the layer). From this it may, apparently, be concluded that the process of aggregation of the particles in the stream (the only process the equilibrium for which is established spontaneously in the layer) is regulated by the condition that the criterial relationship defined by equation (1) remains constant.

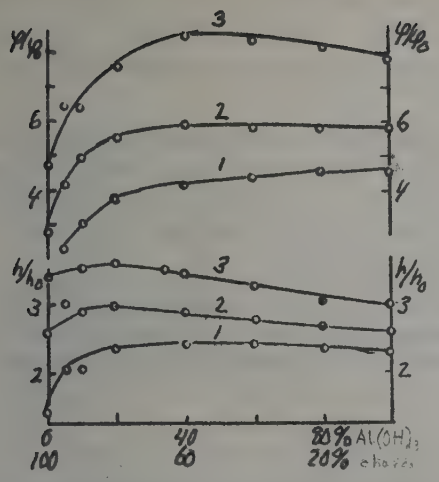

Fig. 2. Dependence of φ/φ_0 and h/h_0 on the composition of a mixture of $Al(OH)_3$ and powdered activated charcoal at rates of flow of the stream entering the layer: 1 — 0.68; 2 — 1.36; 3 — 2.04 mm/sec.

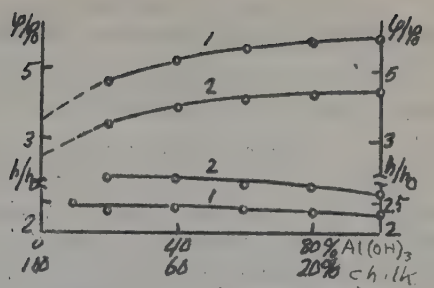

Fig. 3. Dependence of φ/φ_0 and h/h_0 on the composition of $Al(OH)_3$ and chalk powder at rates of flow of the stream entering the layer: 1 — 1.02; 2 — 2.04 mm/sec.

The aggregation and disaggregation processes which take place in accordance with the suspended layer equation, lead in their turn to a definite widening of the layer under the effect of the stream. The rate of flow determines the Euler criterion if the total loading of the apparatus is constant; that is, when $\Delta p = \text{constant}$. Therefore, the degree of widening of the layer; that is, h/h_0 or φ/φ_0 (where φ is the volume of the layer and φ_0 is the sedimentational volume) should remain constant for a given rate of entering flow, independently of the other parameters named above for a suspended layer of mixtures, if the particle shape and, therefore, the packing density of the particles in the precipitate, remains unchanged.

Since the character of the aggregation is related in some measure to the orientation of the particles during cohesion, it is possible that h/h_0 or φ/φ_0 will be constant only if the shape factor, which reflects this orientation in mixtures, remains constant. Figures 2-4 show the dependence of values of φ/φ_0 and h/h_0 on the composition of mixtures of hydroxides of aluminum and iron with powdered activated charcoal and chalk. These data show that the ratio h/h_0 does in fact increase only very slowly with increasing proportion of the powdered component in the mixture from 0 to 80-90%.

As Figures 3 and 4 show, the value of φ/φ_0 remains more constant when the composition of the mixture varies, than does h/h_0. The explanation for this is that in a conical diffuser the widening of the layer is not proportional to the increase in its height.

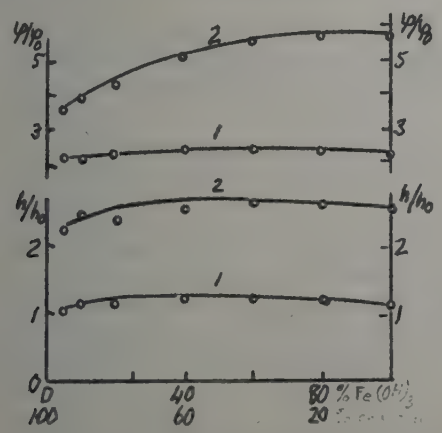

Fig. 4. Dependence of φ/φ_0 and h/h_0 on the composition of mixtures of $Fe(OH)_3$ and activated charcoal at rates of flow of the stream entering the layer: 1 — 0.68; 2 — 2.04 mm/sec.

The results of the present study show that constancy of the degree of widening of a suspended layer formed by mixtures of heterogeneous highly dispersed substances in which supermicellar structure formation and cohesion effects are pronounced, does not depend on the ratio of the components, the degree of dispersion of the particles, their density, and the value of the Reynolds criterion at the entry into the layer. The degree of widening of the suspended layer is also not in any simple relationship with the rate of flow of the stream leaving the suspended layer in a conical diffuser. Our data indicate that φ/φ_0 or h/h_0 depend only on the rate of flow of the stream entering the layer, and possibly vary to some extent with changes in the shape factor of particles aggregated in the layer.

SUMMARY

1. The formation of suspended layers of mixtures of freshly precipitated hydroxides of aluminum and iron with powdered activated charcoal and chalk has been studied.

2. It is shown that the degree of dispersion of the secondary particles of the mixture formed in the stream depends on the composition of the mixture.

3. It is shown that over a wide range of ratios of the components in the mixtures the shape factor of the secondary particles formed in the stream as the result of aggregation is practically unchanged, but differs appreciably from the shape factor of particles in suspended layers of the separate components. It is established that the shape factor has the lowest value in suspended layers of pure hydroxides of aluminum and iron. The shape factor of particles in a suspended layer of powdered activated charcoal approaches unity.

4. It is established that the degree of widening of a suspended layer for the mixtures studied remains practically constant with variations of the ratio of the components up to 80-90% charcoal in the mixture, despite changes in the density of the disperse phase, size of the particles which form the layer, Reynolds number, and the rate of flow of the stream leaving the layer.

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Received July 2, 1953

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INVESTIGATION OF THE STRUCTURE OF SYNTHETIC POLYAMIDES

IV. X-RAY DATA ON STRUCTURAL TRANSFORMATIONS

N. V. Mikhailov and V. O. Klesman

X-ray study of the structure of fiber-forming polymers, particularly of natural origin, commenced a relatively long time ago. There are numerous monographs which give data on the structure of proteins (natural silk, wool, etc. [1]), cellulose and its derivatives, and also other polymers [2]. X-ray studies of synthetic polyamides, however, were started only very recently and consisted chiefly of geometrical descriptions of their crystalline structure. Experience with many similar studies of cellulose and its derivatives [3] shows that this direction is not very fruitful, and in any case the data obtained are not sufficient for a definite solution of the problem of the phase state of the polymer. In our view it is more important to establish by this method a relationship between the structure formation and conditions of setting of the melt or of precipitation of the polymer from solution.

Our work consisted of X-ray investigations of the structure of polyamides in the form of fibers, films and resins, in relation to thermal treatment, deformation, and the molecular weight of the polyamide. In view of the aims of the investigation, we did not make a full calculation of the X-ray data and limited ourselves to the utilization of the X-ray diagram to determine the interplane distances and to evaluate qualitatively the changes occurring in the polyamide structure. Polyamide fibers without stretch and drawn to 100, 200, 225, 300 and 315% were studied. The X-ray diagrams for these polyamide fibers are shown in Figure 1.

The diagram of the original unstretched polyamide fiber (Figure 1, a) shows two interference rings, one of which shows strong and the other weak blackening. The diameters of the rings measured from the maximum intensities correspond to the following interplanar distances: $d_1 = 8.44$ A and $d_2 = 4.32$ Å*.

The interference picture on the X-ray diagram of a polyamide fiber drawn to 100% (Figure 1, b) differs little from the corresponding picture for unstretched fiber. The same external ring is retained on the diagram, but the formation of small equatorial spots is also observed. The inner ring splits into two arcs which appear as the result of reflection from planes perpendicular to the fiber axis. The same may be said of polyamide fiber drawn to 200 and 225%. These X-ray diagrams (Figure 1, c) show relatively more distinctly the same interferences, corresponding to the following interplanar distances: $d_1 = 8.42$ Å, $d_2 = 4.33$ Å.

A different interference picture is characteristic of fiber drawn to 300% and over (Figure 1, d). The ring-shaped large diameter interference is gathered at the equator in two intense patches. These patches correspond to interplanar distances of 4.50 and 3.86 Å. Instead of the weak diffuse ring, 8 spots of varying intensity are seen. It may be noted from the X-ray diagrams obtained that in the case of the original isotropic polyamide fiber the X-ray picture is relatively deficient in interferences.

An appreciable change of this in the sense of the formation of a texture can only be seen in specimens of fibers with a sufficiently high degree of stretch. The diffuse state of the X-ray interferences in the original polyamide is apparently due to defective crystalline regions, and possibly also to the presence of disordered regions in the polyamide. The result of an external stretching force on the polyamide is, so to speak, a separation of this diffuse interference ring. By the separation of the interference line is meant the development (or "clarification"), in the stretching process, of the interference characteristic of the polyamide, which, when the specimen is in the isotropic state, is masked by incoherent scattering of the X-rays from the disordered regions in the polyamide structure.

It may be concluded from this that the polyamide fiber in its original isotropic state has a relatively high degree of order of its molecular chains or regions of them. Therefore, the "separation" of the interference should be due to the fact that mechanical stretching creates conditions for the fusion of crystalline regions and the new formation of a more ordered structure with the same symmetry parameters, which naturally leads to a smaller degree of defectiveness and consequently to a clarification of the X-ray picture with removal of incoherent scattering.

*d was found from data obtained by photometric measurement of the X-ray diagrams with a recording photometer.

This explanation is in agreement with the views put forward by Kargin and Sogolova [4] in their study of the action of mechanical forces on polyamides. Re-melting of the polymer takes place under the action of a definite mechanical force, which, according to our data, arises after 200% deformation of a macrospecimen is attained. As is known, structure formation in polymers depends to a considerable extent, on the rate of the process. For example, the rapid cooling of a polymer melt creates conditions for a sharp increase of molecular interaction and a lowering of the thermal motion of the links in the molecular chains in the sample studied. By means of such cooling of a polymer melt it is possible to obtain a rapid transition from the visco-fluid to the solid (glassy)state of the substance, similar to the transition of liquid low-molecular substances into the supercooled solid state. For the formation of a crystalline structure in a polymer, on the other hand, conditions are necessary in which the interaction between the molecules should not vary too rapidly and the molecules should retain sufficient flexibility for a time sufficient for intra- and intermolecular regroupings to take place.

We attempted, using polycaprolactam, to achieve conditions which favor the production of various structural modifications, and also to effect interconversion of these polyamide structures in conditions which are practicable in the laboratory. We obtained crystalline specimens of the polyamide by slow cooling of the melt, and supercooled specimens by rapid cooling of the polyamide melt in a thin layer (Figure 2).

The X-ray diagrams of the crystalline preparations show a relatively full interference picture, which indicates a maximum ordered state of the polymer. The X-ray diagrams (Figure 2, a) clearly show sharp interference rings of considerable intensity. This specimen of polyamide corresponds to a range of interplanar distances: $d_1 = 4.95$ Å; $d_2 = 4.57$ Å; $d_3 = 4.21$ Å; $d_4 = 3.78$ Å. The X-ray diagrams also show other interferences, corresponding to small identity periods, but determination of their interplanar distances is difficult in view of their low intensity. Such an X-ray picture is also shown by specimens of low molecular weight, obtained by fractional precipitation of the polyamide from solution, and also specimens obtained by free evaporation of the solvent from a solution of polycaprolactam (Figure 3 a, and b).

It was established by a comparative evaluation of the X-ray diagrams of specimens of different molecular weight that as the molecular weight decreases, so the ring interferences become more narrow and sharp. An explanation for this is that the shorter chains are capable of forming a more regular crystalline lattice, which naturally decreases the defectiveness of the structure and so leads to a more sharp X-ray diagram.

The examples discussed above showed that under definite conditions a polyamide may be obtained with varying degrees of defectiveness of crystal structure. However, this defectiveness is shown in the X-ray diagrams in a very peculiar way; it not only decreases the number of reflections on the diagrams, but it also masks them and creates the appearance of a disordered amorphous structure in the original polyamide specimens. Indeed, the interference picture in X-ray diagrams of such specimens is less sharp and poor in reflections in a direction perpendicular to the equator by comparison with other crystalline substances such as polyethylene.

In contrast to the conditions of slow cooling of a polyamide melt or of evaporation of solvent from a solution, when opaque polyamide films or threads are formed, we succeeded in obtaining a clear film by rapid cooling of a polyamide melt. As was already shown earlier, the X-ray diagram of such a film (Figure 2, b) differs substantially from the X-ray picture of crystalline specimens (Figure 2, a). The X-ray diagram of this specimen (Figure 2, b) shows two broad diffuse interferences. It might be supposed that a supercooled polyamide melt should crystallize at room temperature However, this was not confirmed by the X-ray diagram, which showed that the structure formed was retained during twelve hours' exposure. This observation is confirmed by X-ray structure data for a rapidly cooled specimen, which was then heated for three hours at 110° followed by natural cooling (Figure 4).

The X-ray diagram (Figure 4, a) shows a sharply defined ring inside the diffuse ring which existed previously in the original specimen (Figure 2, b). Evidently, heating for three hours at 110° does not provide all the conditions for the regrouping of the molecules which is needed for crystallization of the polymer. If, however, the supercooled specimen was heated for the same period of time, but at 175-180°, then the X-ray diagram of this specimen, shown in Figure 4, b, becomes more distinct and more rich in interferences. The X-ray diagram of this specimen strongly resembles that of a crystalline specimen obtained by slow cooling of a melt or evaporation of a solvent, and has the same four interference rings, although these are less sharp. This confirms that the polyamide specimen obtained by rapid cooling of the melt corresponds to a nonequilibrium supercooled glassy state of the polyamide, which passes into the equilibrium crystalline state on heating to 175-180°.

In the present case, the temperature is a factor which varies the kinetics of the transition from the nonequilibrium to the equilibrium state. Heating favors the considerable acceleration of the displacement of the polyamide links, which was retarded by the rapid cooling, and the formation of a spatial ordered structure is facilitated.

Therefore, it may be considered, on the basis of the data of X-ray structure analysis, that the polyamide may

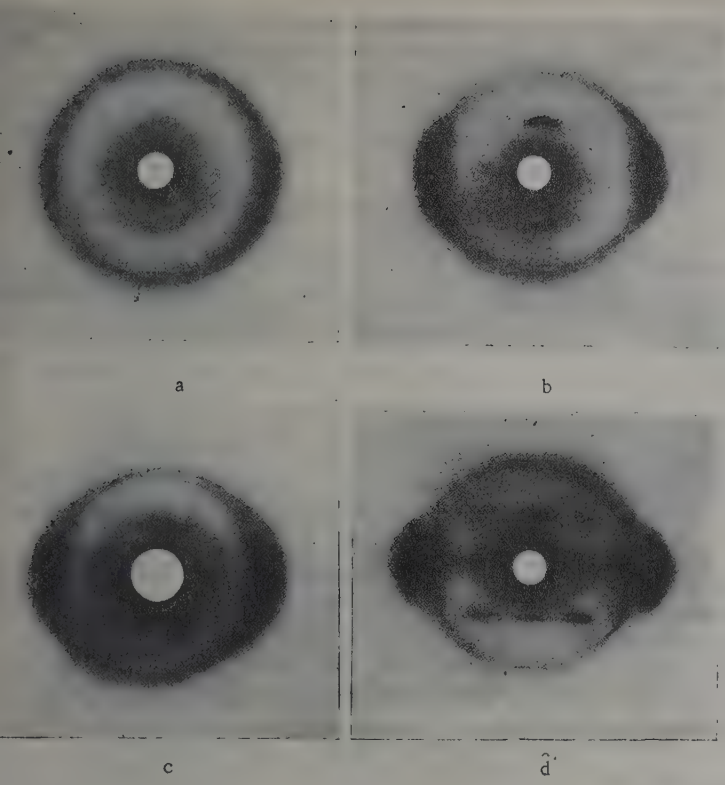

Fig. 1. X-Ray diagram of polyamide fibers: a) unstretched fiber; b) fiber drawn to 100%; c) to 200 and 225%; and d) to 300 and 315%.

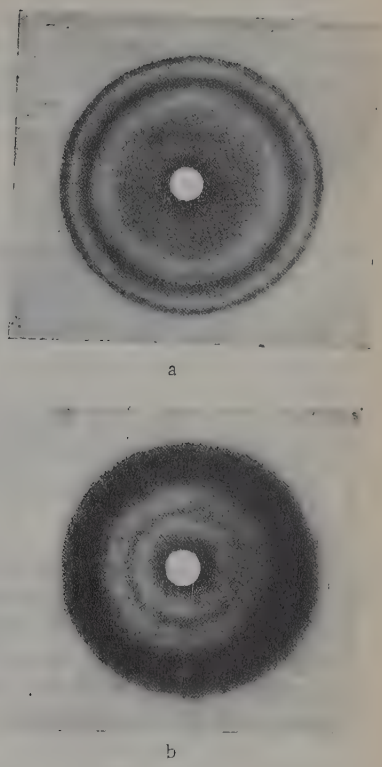

Fig. 2. X-Ray diagrams of structurally different polymer specimens: a) for white opaque polyamide film (crystalline specimen); b) for transparent polyamide film (supercooled amorphous specimen).

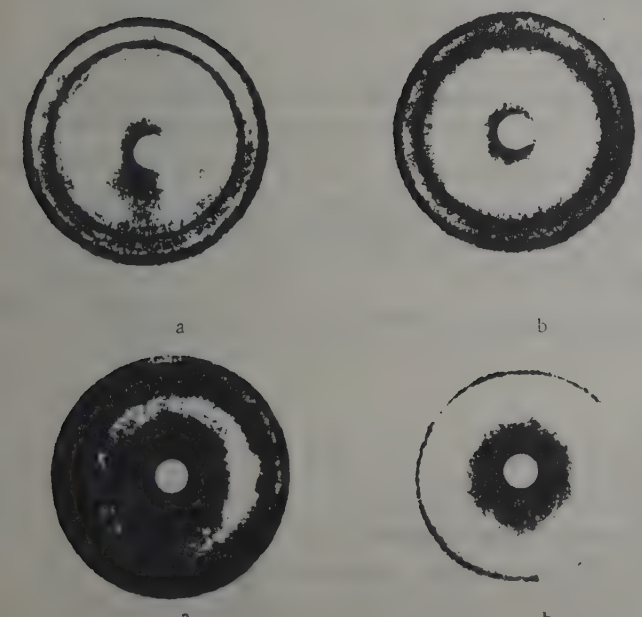

Fig. 3. X-Ray diagrams of polyamide specimens of different molecular weight. 1) First; b) 6th fraction of polycaprolactam.

Fig. 4. X-ray diagrams of polyamide specimens obtained by sudden cooling of the polymer melt and then heated for 3 hours: a) at 110°; b) at 175-180°.

exist in two interconvertible forms: the crystalline and the glassy (amorphous). To study the effect of mechanical forces on the crystallization of supercooled polyamide, we investigated the effect of stretching on changes in the structure of the glassy polyamide. This is also of importance for comparison of the behavior of these two structural modifications on stretching. The X-ray diagrams of both stretched specimens were obtained, as far as possible, under the same conditions. Examination of the X-ray diagrams of these specimens shows that the number of reflections is the same in both, but their sharpness differs, and is more intense for the stretched supercooled specimen, which indicates greater structural homogeneity. The interplanar distances also differ beyond the limits of accuracy of the measurements:

1) For stretched supercooled specimen: $d_1 = 7.73$ Å; $d_2 = 4.95$ Å; $d_3 = 4.41$ Å; $d_4 = 3.79$ Å.

2) For stretched crystalline fiber: $d_1 = 8.48$ Å; $d_2 = 4.50$ Å; $d_3 = 3.86$ Å.

The table shows a summary of the results of determinations of interplanar distances d for polyamides of different structure, obtained under different conditions.

TABLE

Interplanar Distances for Polyamides of Different Structure.
(Numbers of the interferences are counted from the center spot of the X-ray diagram.)

Type of polyamide specimen	1		2		3		4	
	Intensity	Å	Intensity	Å	Intensity	Å	Intensity	Å
Crystalline specimen—white opaque polyamide film	vw	4.95	vw	4.57	vw	4.21	w	3.78
Crystalline specimen—low viscosity fraction of the polymer; obtained from solution	w	8.05	w	4.53	w	4.95	w	3.79
Glassy (amorphous) specimen—transparent film	w	8.29	w	4.23	—	—	—	—
Glassy (amorphous) polyamide specimen after heating at 110° for three hours	s	4.52	vw	4.32	w	4.20	—	—
Glassy (amorphous) specimen after heating at 170-180° for three hours	m	4.53	m	3.77	w	4.52	—	—

Note: s = strong, m = medium, w = weak, vw = very weak intensity.

From a comparison of the interplanar distances for polyamides of different structure given in the Table, it may be concluded that the observed variation of the diffractional picture in the samples of synthetic polyamides studied is due to kinetic peculiarities in their structure formation.

SUMMARY

1. It is shown that synthetic polyamides can exist in two structural modifications: the crystalline and the amorphous (glassy) of which the first corresponds to the opaque (mat) and the second to the transparent state.

2. The structural modifications found in the synthetic polyamides are capable of reversible interconversion.

3. Study of the structural transformations in synthetic polyamides showed that the crystalline modification represents the equilibrium state, as the amorphous modification is a supercooled melt retarded by strong intermolecular interaction, and represents a theoretically nonequilibrium state.

In conclusion, we take the opportunity to express our gratitude to X-ray technologist P. M. Larionov for assistance in the work.

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Received July 8, 1953

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CHARACTER OF THE RHEOLOGICAL CURVES OF PARAFFINIC PETROLEUMS WITH DIFFERENT RESIN CONTENTS

V. F. Nezhevenko

In strata conditions petroleum apparently consists of a completely homogeneous complex mixture of various hydrocarbons, in which paraffin and resins form a true solution containing different amounts of dissolved gas. When the petroleum reaches the surface from the well, as the result of evolution of gas and of the decrease in temperature, the equilibrium between the different classes of hydrocarbons is disturbed in the direction of a decrease in the solubility of solid paraffins. The formation of a solid phase of paraffinic hydrocarbons in the petroleum leads to the appearance of anomalous viscosity and thixotropy.

Sufficient attention has not been paid up to the present to studies of anomalous viscosity and thixotropy of paraffinic petroleums. The available data in the literature [1] indicate a dependence of the viscosity on the velocity gradient for different petroleums, in connection with studies of pumping conditions.

It is known from studies of the low temperature properties of lubricating oils [2] that the appearance of anomalous viscosity in the latter is associated with crystallization processes of paraffins. It is also known [3] that surface-active substances retard crystallization of paraffins in petroleum products, lowering their solidification temperature and displacing the region of anomalous viscosity into the zone of lower temperatures [4]. Resins in petroleum are surface-active compounds which should undoubtedly strongly affect the crystallization processes of paraffins in petroleum.

This paper presents the results of a study carried out in order to elucidate the effect of resins on the nature of the rheological curves of paraffinic hydrocarbons.

EXPERIMENTAL

The investigations were carried out with three petroleums, with different resin contents.

The physico-chemical characteristics of the petroleums studied are briefly given in the Table.

The rheological curves of petroleums 1 and 2 were determined with an Ubbelohde capillary viscosimeter, and the curves for petroleum 3 with a Volarovich rotational viscosimeter (model RV-7). The following procedure was adopted for both types of viscosimeters: the experiment was started at the minimum pressure capable of producing flow of petroleum in the viscosimeter (or at the minimum load required to rotate the inner cylinder of the viscosimeter). Measurements at this pressure were made several times, until constant readings were obtained, indicating complete destruction of the structure at the given pressure. The pressure was then progressively increased and the measurements were made in the same way for each new pressure.

The pressure was increased until further increase did not affect the value of the viscosity (in the case of the capillary viscosimeter, till the product of the pressure and the time of efflux became constant), that is, until the structure formed was completely destroyed. The experiment was then carried out in the reverse direction, with a gradual decrease of pressure to the minimum value which still caused the petroleum to flow in the viscosimeter.

For the Ubbelohde viscosimeter, a constant temperature was thermostatically maintained for 30 minutes, and for the Volarovich viscosimeter, 3 hours at 0° and 5 hours at −10° and −20°.

TABLE

Physico-Chemical Characteristics of the Petroleums Studied

Petroleum specimen	Specific gravity of petroleum at 20°	Viscosity of petroleum in poises at 20°	Content of asphaltic-resinous materials in %	Paraffin wax content in % **	Melting point of paraffin in °C	Solidification temperature of petroleum, °C
1	0.803	0.75*	1.7	22.4	50.0	+17
2	0.798	0.03	3.2	5.9	50.5	− 6
3	0.923	2.47	19.0	5.5	50.5	−13

*Viscosity of petroleum with structure destroyed.

**Paraffin wax was determined by the acetone-benzene method of the Groz Research Institute (without destruction).

The experimental data obtained are shown in the form of graphs in $\underline{Q} - \underline{p}$ coordinates for the Ubbelohde viscosimeter, or $\underline{n} - \underline{p}$ coordinates for the Volarovich viscosimeter, where $\underline{Q}$ is the flow of the liquid in the viscosimeter in cm^3/sec; $\underline{n}$ is the rate of rotation of the inner cylinder in rev/sec; $\underline{p}$ is the working pressure in mm water column or the load in grams which causes the inner cylinder of the viscosimeter to rotate.

Petroleum 1 was investigated at 25°. The flow curves for the petroleum with "direct" and "reverse" operation of the viscosimeter (Figure 1) almost coincide as the mechanically destroyed structure is restored in the course of the experiment. It should be noted that petroleum 1 shows anomalous viscosity at 30°.

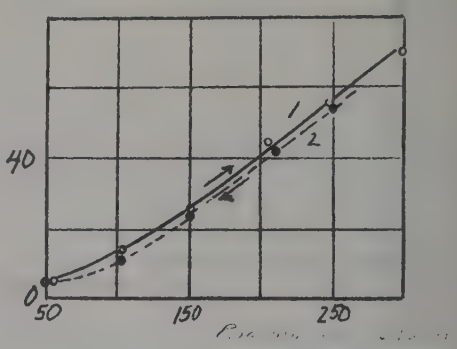

Figure 1. Rheological curves for petroleum 1 at 25°; 1 – with increasing, and 2 – with decreasing pressure.

As the resin content increases (petroleum 2), the solidification temperature decreases, as does the temperature at which anomalous viscosity appears in the petroleum (10).

Petroleum 2 was studied at 0° (Figure 2). The flow curves obtained in direct and reverse operation of the viscosimeter do not coincide but form a thixotropic hysteresis loop, similar to that obtained by Volarovich and Valdman [5] in their study of lubricating oils.

The rheological curve for the petroleum with a destroyed structure is a straight line which passes through the origin, which indicates that the petroleum, as the result of mechanical destruction of the structure formed, becomes a Newtonian liquid. For this petroleum the effect of mechanical stirring is retained for 2-3 hours, after which, the destroyed structure is gradually restored. Petroleums with a considerable resin content are characterized by a relatively low solidification temperature, and also by normal viscosity at positive temperatures. The region of the anomalous viscosity region is, as a rule, below 0° for petroleums with high resin content.

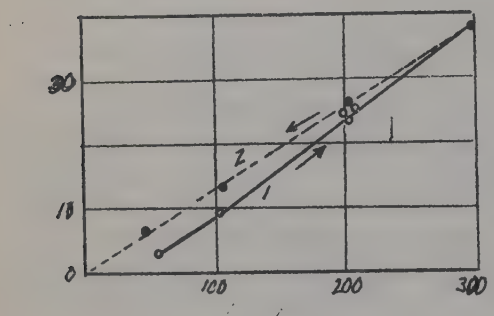

Figure 2. Rheological curves for petroleum 2 at 0°; 1 – with increasing, and 2 – with decreasing pressure.

Figures 3 and 4 show flow curves for petroleum 3 at 0, –10, and –20°. At 0° the petroleum is a Newtonian liquid, the flow curve of which is a straight line passing through the coordinate origin. At –10°, that is, 3° above the solidification temperature of the petroleum, the latter possesses static shear stress and the curves for the direct and reverse operation of the viscosimeter form a thixotropic hysteresis loop. The flow curve of the petroleum with its structure destroyed is a straight line, which passes at low velocity gradients into a curve tending toward the origin.

When the temperature of the experiment is decreased to 20° (Figure 4), the value of the static shear stress of the petroleum increases sharply and the thixotropic hysteresis loop widens. However, the flow curve for the petroleum with its structure destroyed is of the same nature as in the preceding experiment: a straight line which tends to become a curve and passes through the origin.

Thus, the rheological curves for petroleum with a destroyed structure in one case (petroleum 2) consist of straight lines passing through the coordinate origin, and so characterize the petroleum as a Newtonian liquid; in the other case (petroleum 3) these curves have two regions: a linear region, which represents flow under high velocity gradients, and a curvilinear region, for flow at low velocity gradients. Similar curves were also obtained in a study of mineral oils [6].

It should be noted that in light, low-resin petroleums, even at the solidification point, the structure formed has low strength and is easily destroyed during rheological measurements. The petroleum passes into a Newtonian liquid. For high-viscosity resinous petroleums at the solidification temperature, and in some cases also somewhat above, curves of the second type are characteristic. In this case, repeated consecutive experiments at small and large loads do not cause complete destruction of the structure formed, and complete transition of the petroleum into a Newtonian liquid.

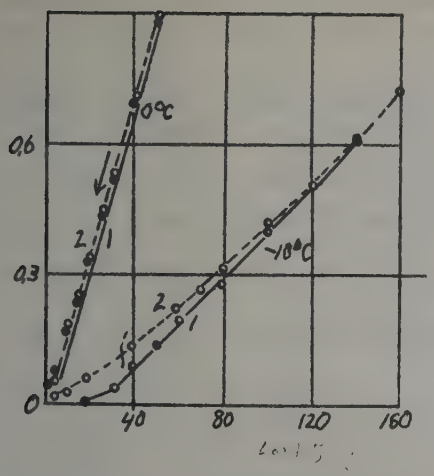

Figure 3. Rheological curves for petroleum 3 at 0°; 1 – with increasing, and 2 – with decreasing load.

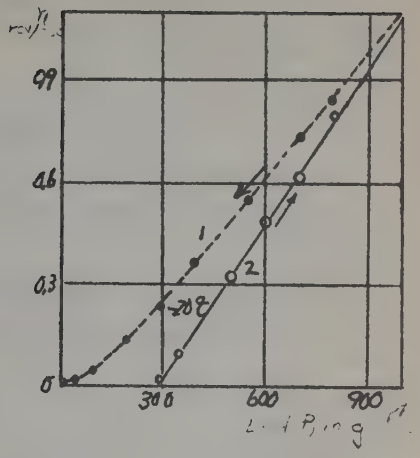

Figure 4. Rheological curves for petroleum 4 at −20°; 1 – with increasing, and 2 – with decreasing load.

A static shear stress arises in petroleum at a temperature a few degrees above the solidification temperature. However, even at the solidification temperature the value of the static shear stress for paraffinic petroleums is insignificant, and comprises 0.1-0.2 g/cm^2.

To verify the results obtained, the viscosity properties of petroleums were investigated direct at three oil fields producing paraffinic petroleum with different resin contents. The results of the studies established that light low-resin petroleums (containing $\sim$3% of asphalto-resinous substances) contain free paraffin wax at the instant of leaving the well. As a result, the oil reaching the surface has anomalous viscosity at 0° and above. The presence of free paraffin wax in the petroleum explains the extensive contamination of the equipment with paraffin wax in oil wells producing low-resin paraffinic petroleums.

In oil wells in which petroleum with a higher content (12-14%) of asphalto-resinous materials is obtained, the petroleum leaving the well at 0° and above is a Newtonian liquid. This state of the petroleum, however, is unstable, and when the petroleum is led through pipe lines from the well to the store intensive crystallization of the paraffin takes place in the petroleum.

As a result, commercial petroleum at 0° has a well-defined anomalous viscosity and a higher temperature of solidification than petroleum direct from the well. Finally, in oil wells where heavy, resinous petroleum is obtained (containing up to 20% asphalto-resinous substance) the crystallization processes of the paraffin wax are so retarded from the moment the petroleum is obtained from the well that both the petroleum direct from the well and the commercial petroleum retain the properties of a Newtonian liquid at 0° and above for a prolonged period (10-12 days).

SUMMARY

1. It is established that as the resin content increases, the crystallization rate of paraffin wax in petroleum decreases.

2. Paraffinic, low-resin petroleums show anomalous viscosity at 0° and higher.

3. Paraffinic, high-resin petroleums are Newtonian liquids at positive temperatures (0° and higher). The region of anomalous viscosity for such petroleums is displaced in the region of negative temperatures.

In conclusion, I express my deep gratitude to Professor M. M. Kusakov for valuable advice in the course of the present work.

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Received May 30, 1953

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PECULIARITIES OF THERMAL EXPANSION OF GELS AND HIGH POLYMER SOLUTIONS

II. GELS OF AGAR AND GELATIN

R. E. Neiman

In the first communication [1] it was shown that the coefficient of thermal expansion of gels and solutions of gelatin undergoes an anomalous sudden change at a definite temperature. In the present paper results are given which were obtained in a study of the thermal expansion of agar gels, and also certain new data relating to gelatin. The technique of the measurements is described in the first communication [1].

We must only note in addition that in the new experiments the capacity of the dilatometers was increased to 50-80 ml (with capillary radii of 0.030-0.045 cm). The change of the liquid level in the capillaries was usually from 35 to 70 mm per degree (for different dilatometers). The gel volumes were measured at each 0.5°, and in some cases at 0.1-0.2° intervals.

It was necessary to determine the conditions in which the measured volumes of the gels are at their equilibrium value. Therefore, the kinetics of the establishment of the volume was studied. The dilatometer with the gel was held for a definite time at 5° above or below the temperature of the experiment and was then placed in the thermostat; the establishment of the final volume was observed. These experiments were carried out at different temperatures over the range of 25-40°. The results of one such experiment are shown in Figure 1. The final values are the equilibrium values of the volume, as they are attained quite reversibly both from the higher and from the lower temperatures. At all temperatures the final equilibrium volume became established 15-20 minutes after the gel was placed in the thermostat; this time practically coincides with the time necessary to establish thermal equilibrium. Thus, temperature relaxation of volume is absent in agar gels. This is evidently to be explained by the weak intermolecular interaction between the unattached regions of the chains, as a result of which agar gels do not undergo regroupings which follow relaxational laws.

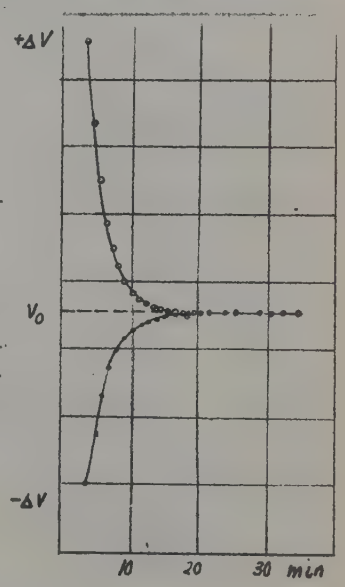

Fig. 1. Kinetics of the establishment of equilibrium volume of 8% agar gel at 25°; $\Delta V = V_T - V_0$ is the difference between the volume V_T, measured at a given instant and the final volume, V_0.

All the results given below relate to the equilibrium values of the volumes. Hysteresis effects do not occur: the curves showing the variation of the volume of the gel with temperature, obtained by heating and by cooling, completely coincide.

Figure 2 shows the curves for the dependence of the coefficient of thermal expansion α of agar gels on temperature. As in the case of gelatin, the coefficient of thermal expansion of agar gels undergoes a sudden change at a definite temperature, reaching a certain maximum. Prolonged storage of the gel has no influence on this effect. To illustrate this, Figure 3 shows the results of experiments lasting a year. During this time, the gels were kept in the dilatometer.

As equilibrium volumes were measured, the jump in the coefficient of thermal expansion could not be caused by kinetic factors, that is, by a definite relationship between the rate at which the experiment was

performed and the rate of the thermal relaxation processes of the gel volume. Thus, in this case the jump in the value of the coefficient of thermal expansion must be associated with a transition from one thermodynamic state to another. Earlier [1] we examined this transition as a critical phenomenon in the sense of the views developed by Semenchenko [2] on generalized critical phenomena, and we put forward the view that in this instance the transition of a solution (of gelatin) into a gel is such a critical phenomenon. However, the results of experiments with agar gels, shown in Figures 2 and 3, cast doubt on the view that the jump of the coefficient of expansion is directly associated with gelation of the solution. The reason is, the jump in the value of α occurs in agar gels at 32-33°, which is below their melting point.

In general, a dilatometric heating curve for the gel was taken, and continued to approximately 36-38°. The gel did not liquefy during this process. Immediately after this, a cooling curve was taken, and a jump of the coefficient of expansion was again found at the same temperature as during heating. These results give reason to suppose that the observed anomaly is caused not by macroscopic modifications of state (gelation, demixing) but by molecular-structural transformations of the polymer molecules.

Thermodynamically similar transformations are apparently of the same nature as those of which the concepts were developed by Semenchenko [3], and which he classifies with generalized critical phenomena, which he terms chemocritical. Urazovsky [4] developed concepts of molecular-polymorphous transformations which take

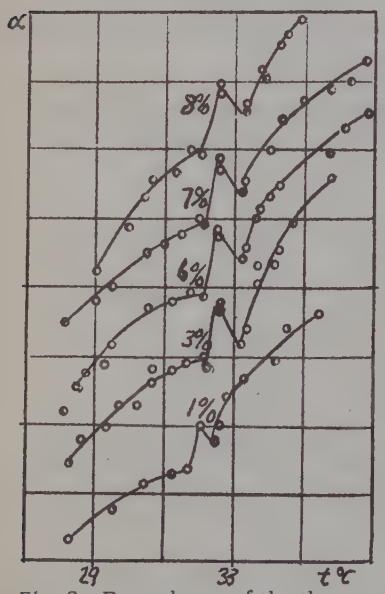

Fig. 2. Dependence of the thermal coefficient α of agar gels on temperature (the ordinates of the curves are displaced relative to each other).

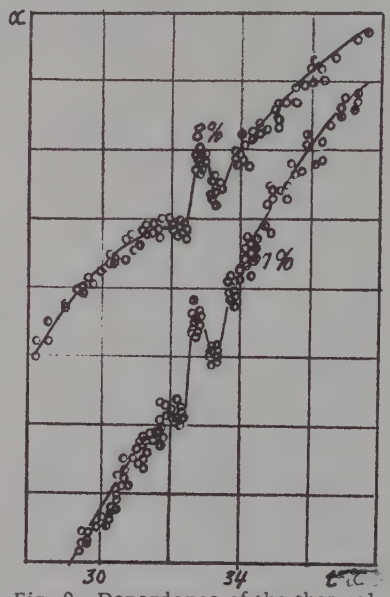

Fig. 3. Dependence of the thermal coefficient α of agar gels on temperature (the ordinates of the curves are displaced relative to each other).

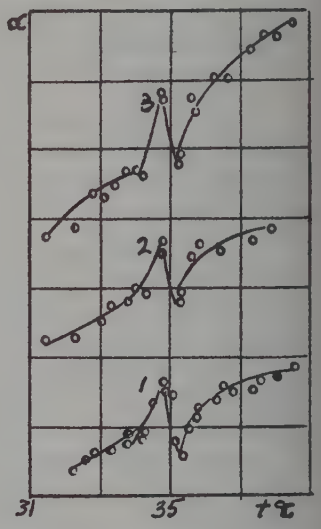

Fig. 4. Dependence of the coefficient of thermal expansion α of 20% gelatin gels on temperature: 1) gel prepared with 3 M urea solution; 2) normal gel; 3) gel tanned with quinone (ordinates of the curves are displaced relative to each other).

place in the liquid phase. It is clear that an attempt to give this or that interpretation for the transformations found by us does not in itself permit definite conclusions to be drawn concerning their molecular mechanism.

In this connection, certain new data obtained by us on the anomalous coefficient of thermal expansion of gelatin gels are of interest. We carried out a series of experiments in which the melting point of gelatin gels was displaced both toward higher and lower temperatures. A sharp increase of the melting point was attained by tanning the gelatin gel with quinone (the quinone was added, in an amount equal to 3% of the gelatin, as an alcoholic solution to the hot solution of gelatin directly in the dilatometer). A decrease of the melting point was produced by preparation of the gel from a 2-3 M solution of urea. The results of one such experiment are shown in Figure 4.

A sharp displacement of the melting point of gelatin gel in either direction has no influence on the observed effect: the jump in the coefficient of expansion is observed at the same temperature for all the gels. Evidently, these experiments confirm that the observed anomaly is not directly associated with gelatine.

SUMMARY

1. An anomaly of the temperature dependence of the coefficient of thermal expansion of agar gels has been found and studied.

2. The view is put forward that this anomaly is due to molecular-structural transformations in the polymer macromolecules (of gelatin and agar).

In conclusion, the author expresses his sincere gratitude to Professor A. V. Nikolaev for his constant interest in the work and for discussion of the results, and to Academician V. A. Kargin for valuable advice given in discussion of the work.

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Received July 15, 1953.

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PLASTICIZATION OF POLYVINYL CHLORIDE BY BUTADIENE-ACRYLONITRILE COPOLYMER

II. CHANGES OF THE PHYSICO-MECHANICAL PROPERTIES OF POLYVINYL CHLORIDE ON THE ADDITION OF VARYING AMOUNTS OF BUTADIENE-ACRYLONITRILE COPOLYMER

R. A. Reznikova, S. S. Voyutsky, and A. D. Zaionchovsky

In the previous paper [1] we examined the effect on the physico-mechanical properties of polyvinyl chloride of the addition of butadiene-acrylonitrile copolymers with different proportions of nitrile and butadiene groups. The present communication deals with a comparison of the effect on the physico-mechanical properties of polyvinyl chloride of the addition of different amounts of a low-molecular plasticizer, dibutyl phthalate, and a high-molecular softener, butadiene-acrylonitrile copolymer containing 36.9% acrylonitrile groups and 63.1% butadiene groups. We established that butadiene-acrylonitrile copolymer with this ratio of groupings has the optimum plasticizing effect on polyvinyl chloride.

As in the previous investigation, the films were prepared by molding in a press by the technique described previously [1]. The films were tested on the dynamometer designed by the Central Research Institute for Leather Substitutes, at 20, 80, 100, and 125°. These temperatures correspond to the softening temperature of polyvinyl chloride, 80°, temperatures of processing and molding of the mixtures, 100-125°, and the normal temperature at which polyvinyl chloride articles are used, 20°.

Effect of plasticizer addition on the tensile strength of polyvinyl chloride films. Figures 1 and 2 show the relationships, found at different temperatures, between the tensile strength of polyvinyl chloride films and their content of dibutyl phthalate and butadiene-acrylonitrile copolymer. The tensile strength in both cases is calculated on the original cross-section of the specimen.

It is seen that at room temperature, plasticized polyvinyl chloride has the high tensile strength of 600 kg/cm^2. With the addition of dibutyl phthalate the interaction between the high polymer molecules decreases. At the same time the viscosity of the substance is lowered, as the mobility of the chains and of the chain links relative to each other increases. As a result, the strength decreases and reaches zero as the pure low molecular plasticizer is approached.

In plasticization with a high molecular softener, the strength curve has the same character. However, the values of the tensile strength are higher over the whole range of concentrations, as butadiene-acrylonitrile copolymer, which has strength in itself, weakens the film to a considerably smaller extent. As the pure butadiene-acrylonitrile copolymer is approached, the strength reaches a value corresponding to that of the high molecular plasticizer – 30 kg/cm^2. Increase of temperature considerably lowers the tensile strength, and at higher temperatures, the difference between the curves for additions of low and high molecular plasticizers decreases considerably.

It was of interest to determine the effect of the plasticizer on the tensile strength calculated on the cross-section of the specimen at break, as such recalculation often leads to a significant change in the shape of the curve. The following equation was used to calculate the tensile strength P_1, relative to the cross-section of the specimen at break:

$$P_1 = P_0(1 + \epsilon),$$

where P_0 is the tensile strength of the film calculated on the original cross-section; ϵ is the relative elongation.

The results obtained are shown in Figures 3 and 4. In both cases, the curves show a sharply defined maximum, which corresponds to a plasticizer content from 30 to 60% in the film. This maximum is more pronounced as the breaking temperature is lower. Evidently, increase of temperature leads to degeneration of the curve because the plasticizing action of the softener in such conditions is masked by thermal plasticization. It is significant that a particularly sharp maximum is seen at 20° on the curve for polyvinyl chloride film plasticized with butadiene-acrylonitrile copolymer.

Thus, with an appropriate method of presentation of results on breaking strength-plasticizer content curves, it is possible to find inflexions and maxima such as are seen in similar curves for residual elongation and extension at break [1, 2]. The presence of such maxima or inflexions on the curve, in our view, is explained by the plasticizing

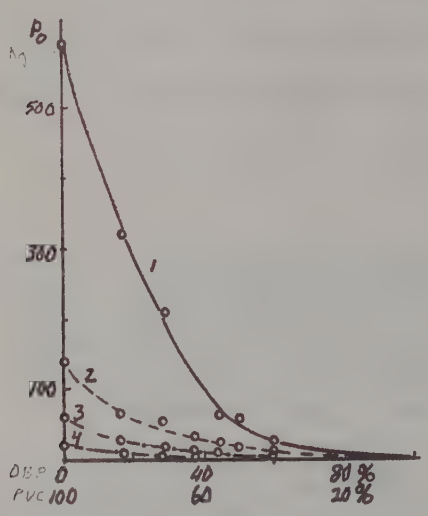

Fig. 1. Dependence of the tensile strength of polyvinyl chloride films on their dibutyl phthalate content (tensile strength calculated on the original cross-section); tensile strength determined at: 1) 20°; 2) 80°; 3) 100°; 4) 125°.

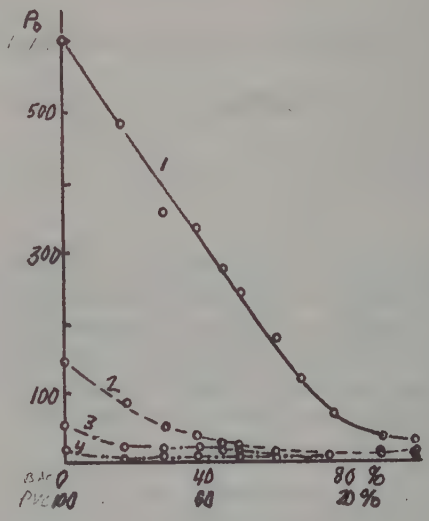

Fig. 2. Dependence of the tensile strength of polyvinyl chloride films on their butadiene-acrylonitrile copolymer content (tensile strength calculated on the original cross-section); tensile strength determined at: 1) 20°; 2) 80°; 3) 100°; 4) 125°.

action of the softener on the polymer, as a result of which the nature of the break changes. As the content of plasticizer in the polymer increases, brittle rupture passes into high-elastic break [3]. Increase of the breaking load in these conditions is due to orientation of the molecular chains and a more uniform distribution of the load between the molecules. On further increase of the plasticizer content, high-elastic break passes into plastic. The tensile strength then decreases as a result of flow of the polymer.

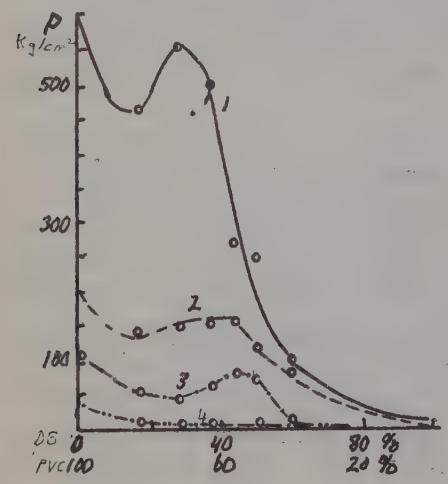

Fig. 3. Dependence of the tensile strength of polyvinyl chloride films on their dibutyl phthalate content (tensile strength calculated on the cross-section at break); tensile strength determined at: 1) 20°; 2) 80° 3) 100°; 4) 125°.

Figures 5 and 6 show the dependence of the tensile strength of polyvinyl chloride films with different contents of dibutyl phthalate and butadiene-acrylonitrile copolymer on the temperature of break. The tensile strength in this case is calculated on the cross-section of the original specimen. The sets of curves shown in Figures 5 and 6 show that the strength of the films falls smoothly with increase of temperature, and gradually approaches zero. The decrease is more pronounced with smaller contents of plasticizer in the film.

Despite the apparently exponential character of the curves, the graphs for $\log P - \frac{1}{T}$ in this case were not linear. This indicates that the dependence of the tensile strength of plasticized polyvinyl chloride film on temperature cannot be expressed by an equation of the Arrhenius type, and that reasoning similar to that used by Dogadkin and Sandomirsky [4] in the interpretation of the temperature dependence of vulcanizate strength is not applicable here.

Effect of plasticizer on the elongation at break and the residual elongation of polyvinyl chloride films. As is seen from Figure 7, which shows the dependence of the elongation at break of polyvinyl chloride films containing different amounts of dibutyl phthalate, on a gradual increase of plasticizer content in the film, approximately up to 50%, the elongation at first increases and then falls, reaching zero. Sokolov and Feldman [2] found curves of a similar form for the relationship between elongation at break and the content of low-molecular plasticizer in polyvinyl chloride films. This form of curve with a maximum is evidently to be explained by the view that with a high content of low-molecular plasticizer the films have a greater capacity for flow, and therefore have low elasticity, which results in their break at small extension.

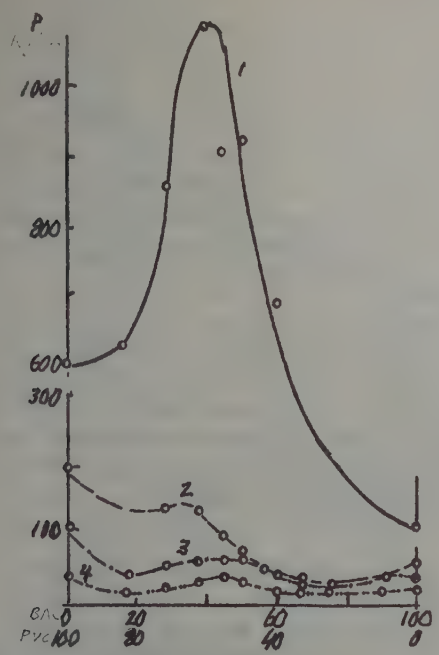

Fig. 4. Dependence of the tensile strength of polyvinyl chloride films on their butadiene-acrylonitrile copolymer content (tensile strength calculated on the cross-section at break); tensile strength determined at: 1) 20°; 2) 80°; 3) 100°; 4) 125°

Comparison of the curves for elongation at break against dibutyl phthalate content for different breaking temperatures shows that the elongation increases at first with increase of temperature, and then falls when the temperature exceeds 80°. Thus, the same relationship is found in temperatature plasticization as in plasticization by the addition of a softener to the polymer.

Different conclusions follow from an examination of Figure 8, which shows the dependence of the elongation at break of polyvinyl chloride films on their content of a high molecular plasticizer, butadiene-acrylonitrile copolymer. In this case, the elongation at break increases with increasing content of butadiene-acrylonitrile copolymer in the film, and reaches a maximum for films of pure butadiene-acrylonitrile copolymer. This is to be expected, as the high molecular plasticizer has a high extensibility in itself. However, at a content of approximately 40-60% of the high molecular plasticizer, all the curves show a plateau, which apparently corresponds to the maximum on the similar curves obtained for polyvinyl chloride plasticized with dibutyl phthalate. Thus, the difference in the form of the curves which show variations

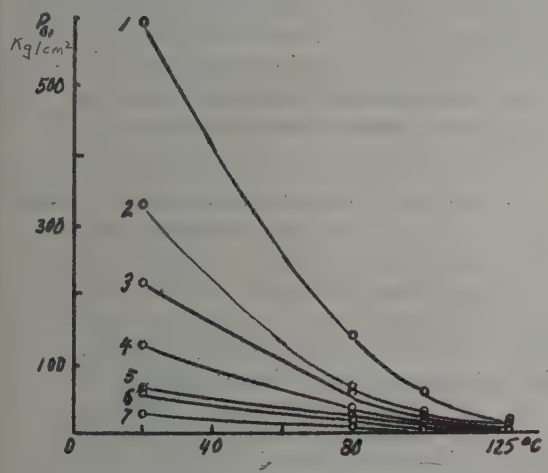

Fig. 5. Dependence of the tensile strength of polyvinyl chloride films with different dibutyl phthalate content on the temperature of break (the tensile strength calculated on the cross-section of the original specimen); 1) film without dibutyl phthalate; 2) film with 16.7% dibutyl phthalate; 3) with 28.6%; 4) with 37.5%; 5) with 44.5%; 6) with 50%; 7) with 60%.

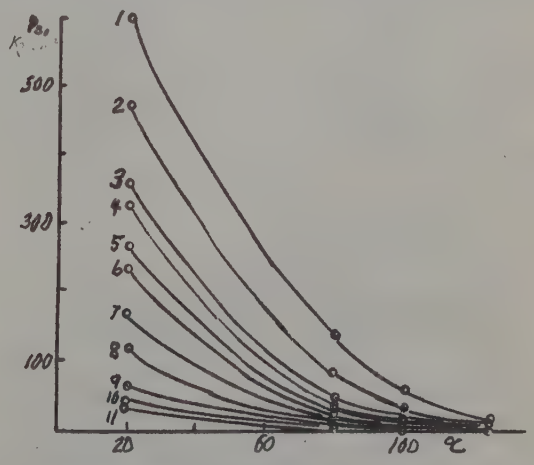

Fig. 6. Dependence of the tensile strength of polyvinyl chloride films with different butadiene-acrylonitrile content on the temperature of break (tensile strength calculated on the cross-section of the original specimen); 1) film without butadiene-acrylonitrile copolymer; 2) film with 16.7% copolymer; 3) with 28.6%; 4) with 37.5% 5) with 44.5%; 6) with 50%; 7) with 60%; 8) with 66.7% 9) with 75%; 10) with 90%; 11) films consisting of butadiene-acrylonitrile copolymer only.

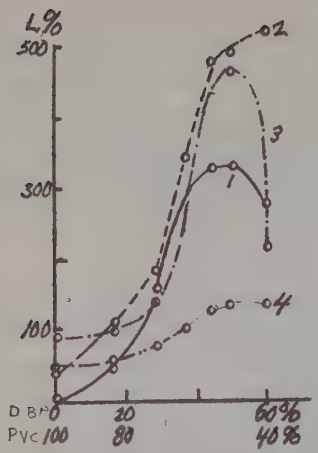

Fig. 7. Dependence of the elongation at break of polyvinyl chloride films on their dibutyl phthalate content: 1) elongation at break, determined at 20°; 2) at 80°; 3) at 100°; 4) at 125°.

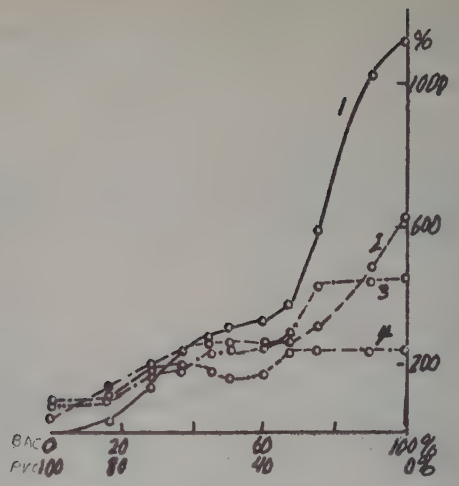

Fig. 8. Dependence of the elongation at break of polyvinyl chloride films on their butadiene-acrylonitrile copolymer content: 1) elongation at break, determined at 20°; 2) at 80°; 3) at 100°; 4) at 125°.

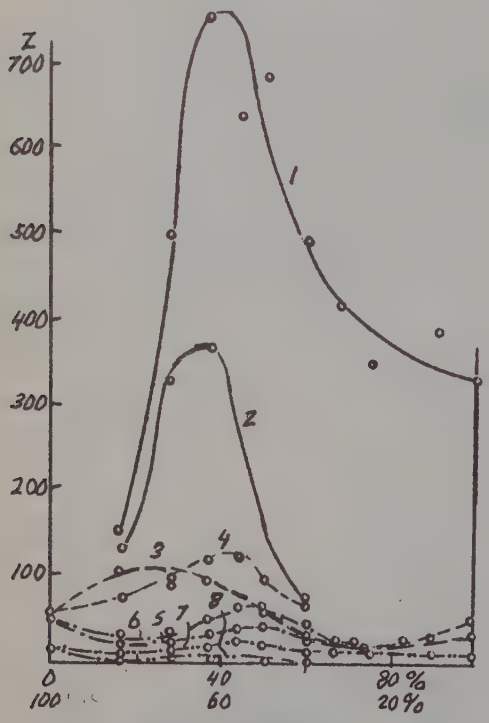

Fig. 9. Dependence of the elasticity product (Z) of polyvinyl chloride films on their plasticizer content; 1), 3), 5), 7) films plasticized with butadiene-acrylonitrile copolymer; tested at 20, 80, 100, and 125° respectively; 2), 4), 6), 8) films plasticized with dibutyl phthalate; tested at 20, 80, 100, and 125° respectively.

of the physico-mechanical properties of polyvinyl chloride with their content of dibutyl phthalates or butadiene-acrylonitrile copolymer is not a fundamental one, but is to be explained only by peculiarities of the mechanical properties of high and low molecular weight plasticizers.

As regards the effect of temperature on the elongation at break, it is seen from Figure 8 that the elongation is greater at higher temperatures when the high molecular plasticizer content is low. When the content of butadiene-acrylonitrile copolymer in the film is high, the situation is reversed. This is to be expected, as with increase of temperature the flow of strongly plasticized films increases considerably, which results in break at small elongations.

Data for the effect of plasticizer content and temperature on the residual elongation are not shown here, as our results were not quite conclusive—the residual elongations measured 1 minute after break can only be termed residual conditionally, as they vanished almost completely with time. We will only note that these curves were of a form analogous to the corresponding curves for the elongation at break.

Effect of plasticizer on the elasticity product of polyvinyl chloride films. Our values for the tensile strength and breaking load of polyvinyl chloride films plasticized with dibutyl phthalate and butadiene-acrylonitrile copolymer make it possible to calculate the corresponding values of the elasticity product Z. As is known, this value, calculated from

the Equation

$$Z = \frac{P_0 a}{100}$$

may give an approximate measure of the energy of elasticity, if the dependence of deformation on stress is approximately linear, as is usually the case for plasticized polyvinyl chloride.

Figure 9 shows the dependence of the elasticity product on the content of the two plasticizers in polyvinyl chloride film. It is seen that in tests carried out at 20°, the elasticity product for films plasticized with butadiene-acrylonitrile copolymer is considerably greater than the elasticity product for films plasticized with dibutyl phthalate. At higher temperatures, the difference between the elasticity products of polyvinyl chloride plasticized with the two plasticizers is less pronounced. This indicates that plasticization with high molecular plasticizers is particularly suitable when the article is used at temperatures which are not too high. At elevated temperatures the effect of plasticization by softeners is masked by thermal plasticization.

It may be seen from the above that from the standpoint of the mechanical properties of the system, it is more appropriate to use high molecular than low molecular plasticizers for polar plastics. The advantage of plasticization by high molecular plasticizers with sufficient polar groups is evidently explained by the fact that such softeners, being able to block polar groups, decrease sufficiently the interaction between the molecular links of the plastic, and at the same time, because of the lower mobility of the molecule as a whole, cause a smaller degree of slippage and relative motion of the macromolecules in the plasticized product. It is also likely that the macromolecules of the plastic and the high molecular plasticizer become interwoven and tangled with each other, and as a result the system plastic-high molecular softener acquires a greater cohesion and elasticity than a system with a low molecular plasticizer.

SUMMARY

1. It is shown that curves for the variation of tensile strength (calculated on the cross section at break), breaking and residual elongation, and the elasticity product, with the content of plasticizer in polyvinyl chloride, show maxima or inflexions. The presence of these maxima or inflexions is explained by the plasticizing action of the softener on the polymer, as a result of which the molecular chains are oriented, the load is distributed more evenly between the chain molecules, and the polymer becomes stronger over a certain range of plasticizer content.

2. It is established that plasticization of polyvinyl chloride with a high molecular softener—butadiene-acrylonitrile copolymer with a sufficient content of polar groups—confers considerably higher physico-mechanical properties on the plasticized product than does plasticization with a low molecular plasticizer—dibutyl phthalate.

3. It is shown that the advantages of plasticization of polyvinyl chloride with a high molecular plasticizer are particularly apparent at moderate temperatures. At elevated temperatures the action of the plasticizer is masked by the temperature plasticization of the polymer and the advantages of the high molecular plasticizer become obscured.

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Received June 8, 1953.

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* See Consultants Bureau Translation, page 207.

STUDY OF THE LAWS OF DEFORMATION OF FILLED RUBBERS*

M. M. Reznikovsky, L. S. Priss, and B. A. Dogadkin

1. The great majority of studies of deformation of rubber relate to unfilled vulcanizates. The results of these studies, which present a considerable scientific interest in many cases, have no direct application in practice, as nearly all technically useful rubbers are made with the use of so-called active fillers, usually highly dispersed carbon blacks. Of the investigations of the properties of filled rubbers, the majority were initiated to elucidate the mechanism of reinforcement, that is, the solution of the question why the introduction of fillers significantly changes the whole complex of the physico-mechanical properties of the rubbers; relatively few studies are devoted to detailed investigation of the mechanical behavior of filled rubbers. First, the work of Patrikeev [1] should be noted; he made a systematic study of the "mechanical memory" effect in filled vulcanizates of natural and synthetic rubbers and was the first to discover a number of remarkable effects. Similar investigations were later carried out by Mullins [2] on filled natural rubbers. The effect of the filler content, the nature of the filler, and the amplitude of deformation on the dynamic properties of filled rubbers, were studied by a number of other authors, for example, Mullins and Fletcher [3, 4].

The present study is devoted to a further elucidation of the laws of deformation of filled rubbers. The materials studied were vulcanizates of SKB and SKS-30 rubbers** with different contents of carbon black. The tests on the specimens were carried out with a float dynamometer [5] and with a Polanyi type rigid dynamometer designed by the Mendeleev All-Union Chemical Society in Moscow. The specimens were kept under thermostatic control during the tests.

2. The difference in the mechanical behavior of filled and unfilled rubbers is easily seen in observations of stress relaxation at a given deformation. In the case of unfilled rubbers elastic equilibrium is established a few hours after extension, so that two readings of the stress taken after a definite arbitrary time interval are equal***. In Bartenev's papers [6] it is shown that for unfilled rubbers the observed equilibrium is close to true equilibrium, which may be confirmed either by variation of the temperature (several heating-cooling cycles lead to reproducible values of the stress at the given temperature), or by variation of the deformation (extension-contraction cycles in the region of deformations close to the original also do not alter the value of the stress at that deformation).

Such experiments, carried out with specimens of filled rubbers, show the very conventional nature of the equilibrium attained when these specimens are held for a definite time at a given deformation, and this conventional nature is shown particularly easily if the specimen is subjected to several extension-contraction cycles. This is illustrated by Figure 1, which shows the dependence of the stress in SKB rubber filled with carbon black on the deformation, time, and temperature.

Section I of Figure 1 shows the curve for constant rate extension up to $\epsilon = 100\%$; Section II shows the relaxation of stress at constant deformation during 60 minutes. At the end of this interval, the stress changes very slowly, but subsequent heating (III) shows that equilibrium is not yet reached. Several heating-cooling cycles lead to the establishment of apparent equilibrium, the conventional nature of which is disclosed if the specimen is subjected to further extension and then contracted again to $\epsilon = 100\%$. The corresponding value of the stress is then found to

*F. M. Kheifets, K. N. Lazareva, and B. I. Gengrinovich, to whom the authors express their gratitude, participated in the experimental part of this work.

**SKB is sodium butadiene rubber; SKS-30 is butadiene-styrene rubber.

***In all real processes, absolute equilibrium is usually not reached and a state sufficiently near to equilibrium is taken as the equilibrium state. The choice of the time interval between the two readings in this case determines the degree of approach of the state reached to the equilibrium state.

be lower than that obtained when the specimen is heated at $\epsilon = 100\%$ (IV). The remaining sections of the graph show the same relationships at $\epsilon = 200\%$, and in the contraction of a specimen extended to $\epsilon = 300\%$, to $\epsilon = 100\%$, the values of the stress are found to be lower than in the contraction of a specimen stretched to $\epsilon = 200\%$. A similar decrease of stress in contraction is also observed in unfilled rubbers, and is due to the existence of elastic hysteresis.

A significant difference between unfilled and filled rubbers in this respect lies in the fact that while in the first case the stress after contraction gradually increases to its original value at that deformation, in the second case this increase takes place more slowly and the established value of the stress is far below the original.

Thus, the stress in filled rubbers which is established as the result of relaxation at constant deformation, essentially depends on the value of the preliminary deformation, and is therefore non-equilibrium. It should be noted that the conventional nature of the elastic equilibrium which is attained as the result of stress relaxation at room and elevated temperatures may also be found on keeping the specimens at the given deformation for a longer period.

3. In true equilibrium, the values of the parameters describing the state of the system do not depend on the states in which the given system existed previously. The rate of approach to equilibrium (determined by the rate of kinetic processes in the system) depends on its structure and on external parameters (temperature, stress, etc.) and in many cases it may be so low that the state of the system does not change appreciably over prolonged periods. Such states may be formally considered as equilibrium states, if to the external parameters which determine the state of true equilibrium we add parameters which characterize the previous history of the system. Examples of such states are provided by the state of the structure of cold-worked metals below the crystallization temperature, the amorphous state of natural rubber cooled rapidly to the glassy temperature, etc. In both these examples, low temperatures strongly retard the kinetic processes in the systems and so fix their non-equilibrium state. Additional parameters which characterize these stable non-equilibrium states are the degree of the cold treatment in the first case, and the initial temperature and the rate of cooling in the second.

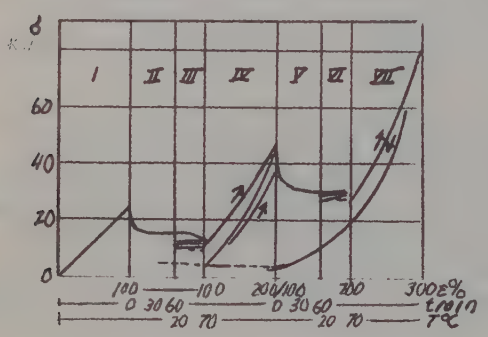

Fig. 1. Conventional nature of the elastic equilibrium in filled rubbers (SKB + 40 parts by weight of channel black); explanations in text.

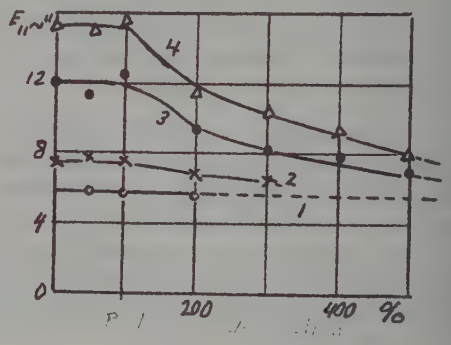

Fig. 2. Dependence of the quasi-equilibrium modulus (determined at $\epsilon = 100\%$) on the value of the preliminary deformation for SKB vulcanizates with different contents of channel black: 1) 0; 2) 10; 3) 20; 4) 40 parts by weight.

From this standpoint it is easy to understand the differences in the mechanical behavior of filled and unfilled rubbers, examined in the previous section. In unfilled rubbers, the establishment of elastic equilibrium (stress relaxation, creep, and elastic after-effects*) are associated with three kinetic processes [7]: rotation of the molecular links about simple carbon bonds, redistribution of stresses in the separate molecular chains, and the regrouping of the sulfur bonds in the vulcanizate with the rupture of individual chains. In the time intervals suitable for measurement only the second process is seen in practice, as the first is completed very rapidly while the third develops very slowly. Thus, stress relaxation in unfilled rubbers leads in several hours to the establishment of elastic equilibrium [6]. Therefore, several extension-contraction cycles close to the deformation at which the equilibrium value of the stress is determined leads, after relaxation, to reproducible values of stress at this deformation.

*The last two terms are taken to mean the gradual establishment of the equilibrium deformation of the specimen at an increase and a decrease of the deformation force, respectively.

In the case of filled rubbers, to the three kinetic processes which determine the rate at which elastic equilibrium is established there is to be added a fourth, which is associated with change of the interaction of the rubber with the filler particles, and the filler particles with each other, as was shown by Dogadkin and Pechkovskaya [7]. This process also takes place very slowly in the case of active fillers, so that the completion of the second relaxation process in this case leads to the establishment of apparent elastic equilibrium. A characteristic feature of the change of the interaction between rubber and filler is its sensitivity to changes of deformation. This can be understood if it is assumed that the rate of the process in question depends significantly on the stresses in the material, and increases rapidly with increase of the latter.

The values of the stress at the established apparent equilibrium will be henceforth termed "quasi-equilibrium" values, and the corresponding values of the modulus, the "quasi-equilibrium modulus" E''_{∞}", both being considered functions of the preliminary deformation.

4. Preliminary experiments on the effect of previous deformations on the quasi-equilibrium modulus, carried out on specimens with varying filler contents, showed that a significant effect is shown only by the maximum deformation which the specimen undergoes. Subsequent deformations of the same magnitude give only insignificant changes of E''_{∞}". Therefore, in the subsequent experiments the pretreatment of the specimens consisted of a single extension and keeping them in the stretched state for 30 seconds. The specimens were tested after fifteen hours' rest. The residual deformations in the specimens which resulted from the preliminary extension were not measured, and the deformation during testing was calculated relative to the length of the specimen before pretreatment.

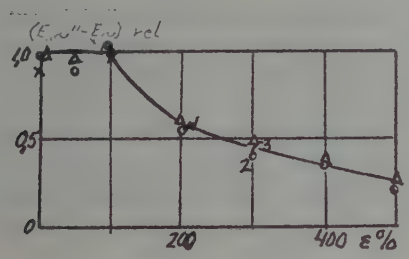

Fig. 3. Relative decrease of the quasi-equilibrium modulus with increase of preliminary deformation for SKB containing channel black: 1) 10; 2) 20; 3) 40; parts by weight.

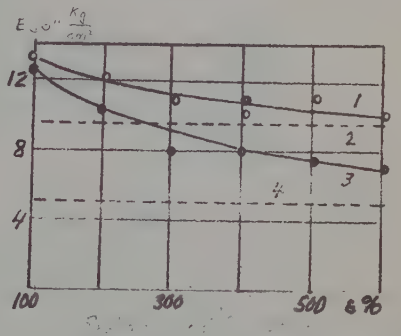

Fig. 4. Dependence of the quasi-equilibrium modulus on the value of the preliminary deformation: 1) SKS-30 + 40 parts by weight of channel black; 2) SKS-30, unfilled; 3) SKB + + 40 parts by weight of channel black; 4) SKB, unfilled.

If only the maximum deformation of the specimen significantly affects E''_{∞}", then the value of E''_{∞}" should not depend on preliminary deformation less than that at which the quasi-equilibrium modulus is determined, as the latter is then the maximum value. The dependence of the quasi-equilibrium modulus on the value of the preliminary deformation for SKB vulcanizates with different contents of channel black fully confirms this. Preliminary deformations less than $\epsilon = 100\%$ (at which the determination of E''_{∞}" was carried out) do not affect the value of the quasi-equilibrium modulus, and only large preliminary deformations decrease it.

It is interesting to note that, for rubbers with different filler contents, the dependence on the preliminary deformation is analogous in the different cases, and the corresponding dependence of the difference of E''_{∞}" $- E_{\infty}$ (where E_{∞} is the equilibrium modulus for unfilled rubber) shows a similarity in the different cases. Figure 3 shows the dependence of the relative values of this difference for the three filled vulcanizates of SKB, shown in Figure 2. It is seen from this Figure that the resemblance holds with a sufficient degree of accuracy. This behavior was observed also in filled vulcanizates of other rubbers, and also in dynamic tests (in this case instead of E''_{∞}" $- E_{\infty}$ the difference of $E_{dyn} - E_{\infty}$ is examined).

Fletcher and Gent [4] studied the decrease of the dynamic modulus for filled rubbers based on natural rubber in alternating shearing deformations of small amplitude (up to 3%) and they found that the decrease of the dynamic modulus with increase of deformation amplitude proceeds analogously in rubbers with different filler contents and with different fillers, if the specimens are fully vulcanized. In specimens which were not vulcanized completely, there was a more rapid decrease of dynamic modulus with amplitude than was to be expected. From our

point of view, the observed deviations are due only to the fact that incompletely vulcanized rubbers have lower values of E_{∞}, and it is to be expected that the dependence of the difference of $E_{dyn} - E_{\infty}$ on the deformation amplitude for these vulcanizates will resemble that for rubbers with different filler content with normal vulcanization time.

The above discussion shows the very great significance of the equilibrium modulus of unfilled rubber in describing the behavior of the corresponding filled vulcanizates. The asymptotic tendency of the quasi-equilibrium modulus to reach E_{∞} as the preliminary deformation increases (see Figure 2) gives reason to suppose that the true equilibrium value of the modulus for filled rubbers is equal to E_{∞} or, at least, close to it.

To verify this, experiments were carried out to determine E"$_{\infty}$" after the specimens had been held for a long time at a given deformation (25-35 hours) at a temperature of 80° (the data shown in Figure 2 were obtained after relaxation for 60 minutes at room temperature). The experiments were carried out in atmospheres of air and of nitrogen. Results of determinations on SKB and SKS-30 vulcanizates containing 40 parts by weight of channel black per 100 parts by weight of the rubber are shown in Figure 5. The results obtained for E"$_{\infty}$" are lower than those shown in Figure 2 (which shows the conventional nature of the equilibrium) but still remain above the corresponding values of E_{∞}, shown in Figure 4 by a dotted line. Thus, both increase of the preliminary deformation and increase of the relaxation time (and increase of the temperature at which it occurs) leads to a decrease of the difference of E"$_{\infty}$" $-E_{\infty}$, although the latter never becomes zero. It is noteworthy that the difference of E"$_{\infty}$" $-E_{\infty}$ is less for filled vulcanizates of SKS-30 than for vulcanizates based on SKB, and decreases more rapidly with increasing preliminary deformation, which is apparently evidence of a weaker interaction between the rubber and filler in this case.

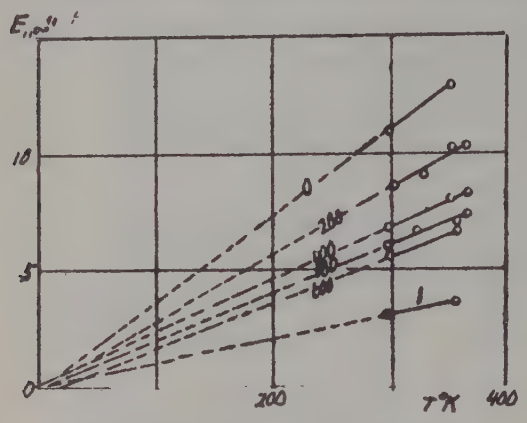

Fig. 5. The dependence of the quasi-equilibrium modulus on temperature for SKB vulcanizates with 40 parts by weight of channel black (numerals on the lines indicate the value of the preliminary deformation; 1) unfilled vulcanizate).

By variation of the temperature in the determination of the quasi-equilibrium modulus its dependence on temperature was determined. As is seen from Figure 5, which shows data for filled SKB vulcanizates which underwent various pretreatments, the lines for the temperature dependence show good extrapolation to absolute zero temperature. This shows that the elasticity of filled rubbers, as well as unfilled, is due to the elasticity of the molecular chains, the rigidity of which, however, increases in the case of filled rubbers due to the interaction between rubber and filler and to the existence of a thixotropic carbon structure.

5. The peculiarities of the mechanical behavior of filled rubbers examined in the preceding sections indicate that these substances are very sensitive to pretreatment. This is shown particularly clearly on the extension curves* for specimens subjected to different pretreatment. Such sets of curves for extension at constant rate for filled SKB and SKS-30 rubbers are shown in Figure 6. The values of the maximum deformations in the pretreatment are shown by numerals.

A characteristic peculiarity of these curves is that they can all be clearly divided into two portions, covering the regions of initial and repeated deformations respectively. While in the repeated deformation region the course of the curves is such that the stresses corresponding to a given deformation are lower with increasing preliminary deformation of the specimen, in the region of initial deformations (that is, for deformations in excess of the maximum deformation in pretreatment) the course of the curves

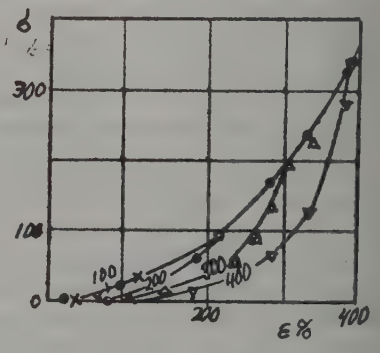

Fig. 6. Curves for the extension of pretreated specimens: SKB + 40 parts by weight of channel black (numerals on the curves indicate the value of the preliminary deformation).

*Structural changes in filled rubbers under the influence of heat and deformation were studied by Dogadkin and Pechkovskaya [7] by changes in the electrical conductivity of the rubbers.

does not depend on the preliminary deformations.

As was already stated, this effect was first studied by Patrikeev [1] and then by Mullins [2]. The data given above fully confirm the results of these authors and give every reason for considering the law as a general one.

The fact that the form of the extension curve in the region of initial deformations does not depend on the pretreatment may be considered as an indication that the properties of a stretched specimen are independent of the preliminary deformations in this region. An interesting illustration of this is the fact, already noted previously by other workers, that the tensile strength of filled rubber does not change as the result of preliminary deformations (if their number is not too great).

In studying the effect of preliminary deformation on tensile strength, we carried out experiments on repeated extension of the specimens after break (tests were made on the shortened strips which were portions of the specimen originally broken). Results for rubber based on SKB with different contents of channel black are shown in Figure 7. The behavior of a previously broken specimen on repeated extension is interesting because the curves for its

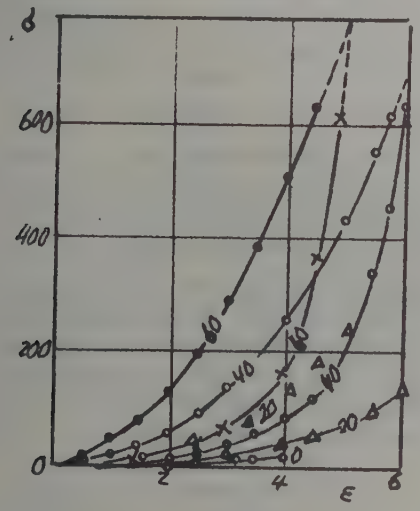

Fig. 7. Effect of preliminary deformation on the tensile strength of rubbers based on SKB (numerals on curves show the content of channel black in parts by weight per 100 parts by weight of rubber).

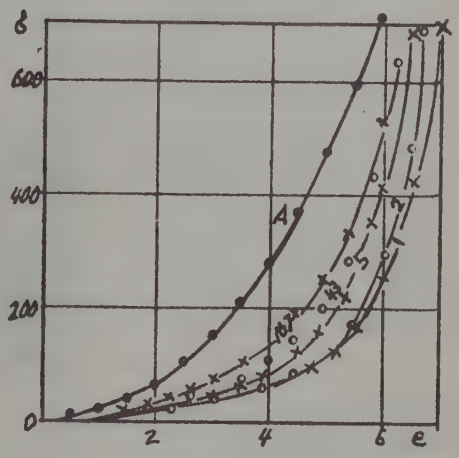

Fig. 8. Effect of rest on the form of the constant rate extension curves; SKB + 40 parts by weight of channel black (numerals on curves — time of rest in days; A) first extension.

extension in the region of small deformations practically coincide with the extension curve for unfilled vulcanizate, diverge strongly from it at extensions close to the breaking extension, and cross the curve for the first extension near the point of break.

A study of the effect of pretreatment on the mechanical properties of filled rubbers would be incomplete without an examination of the restoration of the initial mechanical properties with time. The observations made showed that this restoration occurs very slowly. Figure 8 shows curves for the repeated extension of a number of specimens of filled rubber based on SKB (with 40 parts of channel black by weight), which differed in the duration of the resting period between the first and the repeated extensions (the numerals on the curves show the rest time in days; the upper curve represents the first extension). For all specimens the first extension was taken up to the breaking extension. It is seen from Figure 8 that even very prolonged rest (5.5 months) at room temperature restores the original properties of the material far from completely (less than 50%).

6. The important role of E_{∞} in the characterization of the mechanical properties of filled rubbers is shown particularly clearly in their dynamic properties. The basic characteristics of a material in dynamic tests are the dynamic modulus E_{dyn} and the losses per cycle in unit volume. The latter are termed the "modulus of friction", k, which is introduced, by analogy with the dynamic modulus, by means of the Equation

$$\Delta W = k\epsilon_0^2 \text{ *}, \qquad (1)$$

*The dynamic modulus is related to the total energy introduced per cycle in unit volume of the material undergoing deformation, by the Equation

$$W = \frac{E_{dyn} \cdot \epsilon_0^2}{2}$$

where ΔW represents the losses per cycle in unit volume of the material undergoing deformation; ϵ_0 is the amplitude of deformation.

For filled rubbers the dynamic modulus and the modulus of friction increase with increase of filler content. We established that

$$\frac{E_{dyn} - E_\infty}{E_{0,\,dyn} - E_\infty} = \frac{k}{k_0} \cong f(c), \qquad (2)$$

where E_{dyn} and k are the dynamic modulus and the modulus of friction for the filled rubber, and $E_{0,\,dyn}$ and k are the values for the corresponding unfilled vulcanizates; c is the content of filler.

If we assume that E_∞ is the true equilibrium modulus for filled rubber, then this relationship indicates that the nonequilibrium portion of the dynamic modulus and the modulus of friction for filled rubber, related to the corresponding values for unfilled rubber within the limits of experimental error, are described by a single function of the filler content. In the present study, further confirmation of this was obtained.

For the determination of E_{dyn} and k, the method of spontaneous contraction of rubber strips was used [9]. The results of these measurements* for SKB and SKS-30 vulcanizates with different contents of channel black are shown in Figure 9.

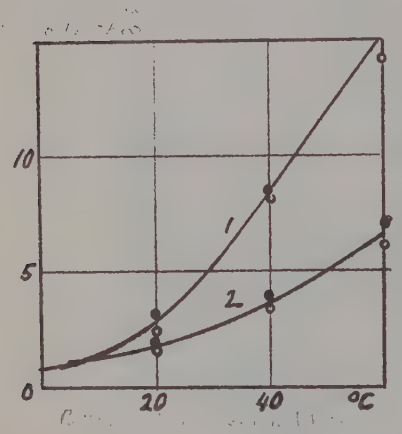

Fig. 9. Dependence of the relative values of the modulus of friction and the non-equilibrium portion of the dynamic modulus on the filler content; 1) SKB; 2) SKS-30.

Study of pretreated specimens showed that previous deformations, while changing the value of $f(c)$ for a given content of filler, do not affect Equation (2). Thus, this Equation is also valid for filled rubbers subjected to preliminary extension, if f is considered as a function of the degree of filling and of the maximum preliminary deformation.

SUMMARY

1. When filled specimens are held for a long time at a given extension, an apparent equilibrium is set up, for the characterization of which the "quasi-equilibrium modulus" — $E_{"\infty"}$, is proposed.

2. The value of the quasi-equilibrium modulus $E_{"\infty"}$ depends on the preliminary deformation of the specimen, the maximum deformation having the most significant effect. Several repeated deformations of the same magnitude have practically the same effect as the first. With increase of the maximum preliminary deformation, the quasi-equilibrium modulus tends asymptotically to the equilibrium modulus E_∞ for the corresponding unfilled vulcanizate.

3. Relative changes of the difference of $E_{"\infty"} - E_\infty$ in relation to the magnitude of the preliminary deformation do not depend on the filler content. Similar behavior is observed with regard to the dynamic modulus, E_{dyn}.

4. The dependence of the relationship $\frac{E_{dyn} - E_\infty}{E_{0,\,dyn} - E_\infty}$ on the filler content and the pretreatment agrees, within the limits of experimental error, with the analogous dependence for relative values of the friction modulus of rubber.

5. The above behavior indicates that the basis of the observed changes in the elastic properties on filling is a sharp increase in the non-equilibrium portion of the stress in the material. The high sensitivity of this portion of the stress to deformation, and the slow restoration during rest, lead to an analogy between filled rubbers and thixotropic colloidal systems with low molecular dispersion media.

*These measurements were carried out by M. K. Khromov, to whom the authors express their sincere gratitude.

6. The linear dependence of the quasi-equilibrium modulus on temperature is extrapolated to absolute zero. This is evidence of the entropy nature of elasticity of filled rubbers.

7. The effect of preliminary deformations on the mechanical properties of filled rubbers is shown most clearly in constant rate extension curves. It is found that the properties of the material in the region of deformations greater than the preliminary do not depend on the preceding deformation. The tensile strength of filled rubbers does not depend on the value of the preliminary deformation.

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Received February 3, 1954.

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*See Consultants Bureau Translation, p. 481.
**See Consultants Bureau Translation, p. 275.
***See Consultants Bureau Translation, p. 375.
****See Consultants Bureau Translation, p. 385.

THEORY OF A SEDIMENTOMETER FOR THE ANALYSIS OF PEAT SUSPENSIONS

N. V. Churayev

Sufficiently accurate and rapid determination of the degree of dispersion of peat is of great significance in peat technology and peat industry. The pipet and hydrostatic methods of sedimentometric analysis used for this purpose [1] have not gained wide application. Therefore, at the present time, the peat industry has neither a sufficiently reliable sedimentometer nor a proved technique for the determination of the dispersion state of peat.

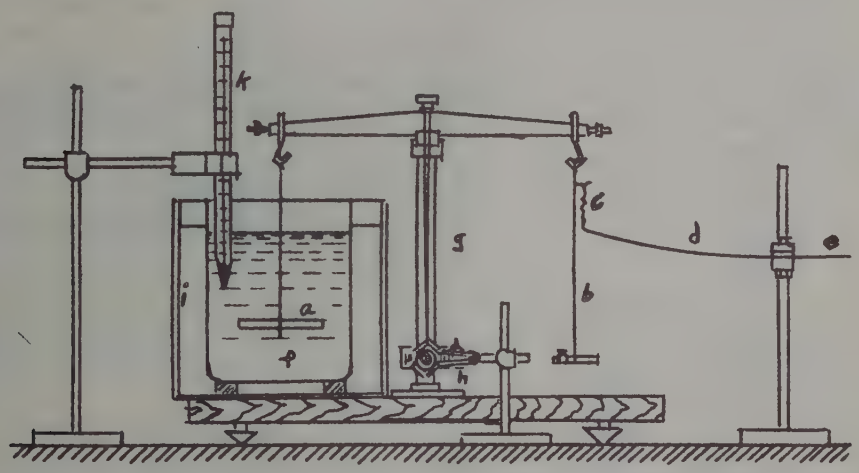

Fig. 1. Scheme of a sedimentometer for peat suspensions (see text).

Peat suspensions have a number of specific properties which must be taken into account in selection of the sedimentometer construction. The small density difference (~ 0.5 g/cm^3) between the dispersion medium (usually water) and the disperse phase, differences in the material composing the particles, which consist of plant fragments of various peat-formers and of humus, the dependence of the true density of the particles on their size, and also the very low concentration of the suspension at which orthokinetic coagulation is absent, – all this creates additional difficulties for accurate sedimentometric analysis of peat.

In our selection of the operating principle for the sedimentometer, we adopted the method proposed by Figurovsky [2], in which the sediment is weighed continuously in a cup connected to an elastic pointer, as being the simplest and most accurate method. However, deformation of the pointer by the weight of the cup, in the case of peat suspension, is many times greater than the deformation under the action of the weight of the settling particles. It was therefore necessary to counterbalance the cup in such a way that deformation of the elastic pointer should occur only by the action of the weight of the settling particles.

The scheme of our proposed peat sedimentometer is shown in Figure 1. It consists of an ordinary technical analytical balance, from the left shoulder of which is suspended a light lacquered aluminum cup a of 10 cm diameter, and from the right shoulder a small cup b with a counterpoise load. One end of a flat watch spring d is attached to the latter by a thread c. The other end of the spring is fixed in a special clamp e, by means of which it is possible to vary its length, and therefore its rigidity and the sensitivity of the apparatus within any required limits. The advantages of a flat spring include a strict adherence to Hooke's law within a

wide range of deformations, the possibility of simple variation of rigidity, and the absence of fatigue effects on repeated changes of load. The length of the spring in our sedimentometer, that is, the distance between the point of attachment in the clamp and the point at which the thread is fixed, is 12.5 cm. When an experiment is performed, 2 liters of peat suspension are poured into the cylinder f of the sedimentometer, diluted to a concentration of 0.02% of the dry material. The left cup of the sedimentometer is immersed to a depth of 10 cm in the suspension, and is counterpoised by suitable weights in the other cup. Readings are taken at definite time intervals of the displacement of the balance pointer g, opposite which a microscope with a scale h is placed. As the particles in the suspension settle in the cup, the beam of the balance turns under their weight and deforms the spring; the magnitude of the deformation is proportional to the weight of the particles settled in the cup. The displacement of the cup in the course of an experiment does not exceed 1-2 mm, and that of the end of the pointer, 2-3 mm. To exclude the effect of convection currents on the course of the sedimentometric analysis, the cylinder with the suspension is placed in a thermostat i. Temperature changes in the suspension during the experiment are recorded by the thermometer k.

It is very important to establish the extent to which the variation of the load on the cup of the sedimentometer balance corresponds to the displacement of the pointer. This correspondence is evidently a criterion of the correct operation of the sedimentometer. Designers of gravimetric sedimentometers (Sven Odén, Starodubtsev [2]) postulated as a necessary condition of the correct operation of the sedimentometer that the balance should be in equilibrium at the moment of reading, which made the construction of the apparatus considerably more complicated and resulted in vibratory motion of the cup in the suspension, which disturbed the course of the experiment.

Let us examine the operation of the sedimentometer described above, the balance beam of which is continuously displaced. Figure 2 shows a diagram of the forces which act on the beam of the sedimentometer balance in the course of the experiment.

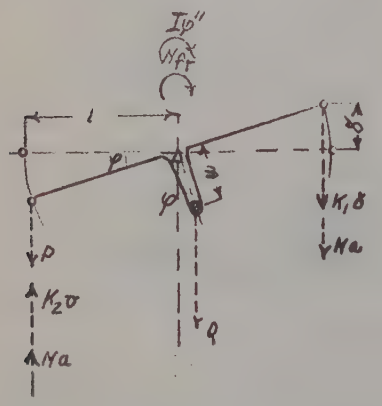

Figure 2. Forces acting on the sedimentometer balance beam (see text).

The following designations are used:

P is the weight of the particles settling in the cup, which is a function of the time;

K_2v is the force of resistance to the movement of the cup in the viscous medium; as the velocities of movement are small, a linear dependence of the resistance on the velocity v is assumed; K_2 is the coefficient of resistance;

Ma is the inertia force of the cup, where M is the mass and a is the acceleration of the cup;

Q is the weight of the beam; m is the distance from the center of oscillation to the center of gravity of the beam;

$I\varphi''$ is the moment of the inertia forces which arise in the rotational movement of the beam; φ is the angular acceleration; I is the moment of inertia of the beam about the center of oscillation;

M_{fr} is the moment of the fractional forces at the pivots;

$K_1\delta$ is the traction force in the flat spring, where δ is the linear deformation and K_1 is the rigidity coefficient of the spring.

We now write the equation for the moments of these forces about the center of oscillation of the balance, namely:

$$Pl\cos\varphi - K_2\varphi' l^2\cos\varphi - 2Mal\cos\varphi - K_1\varphi l^2\cos\varphi - Qm\sin\varphi - I\varphi'' \pm M_{fr} = 0,$$

where l is the shoulder of the balance, and φ is the angle through which the beam turns. As the displacement δ of the cup does not exceed 1-2 mm in the course of the experiment for a shoulder length l = 10 cm, we assume $\sin\varphi = \varphi$ and $\cos\varphi = 1$.

Putting $\varphi = \frac{\delta}{l}$, we have:

$$P \pm \frac{M_{fr}}{l} = \left(\frac{I}{l^2} + 2M\right)\delta'' + K_2\delta' = \left(K_1 + Q\frac{m}{l^2}\right)\delta, \qquad (1)$$

where δ' and δ'' are the first and second derivatives of the displacement δ with respect to time, and $+M_{fr}$ when $\delta' > 0$, and $-M_{fr}$ when $\delta' < 0$.

We must note that essentially the same equation applies to the Figurovsky sedimentometer. In this case the Equation has the form:

$$P \pm \frac{M_{fr}}{l} = M\delta'' + K_2\delta' + K_1\delta.$$

The Equation (1) for the sedimentometer is a nonhomogeneous linear differential equation of the second order with constant coefficients. As is known, the general solution of this equation characterizes the transitional regime, and a particular solution, the established regime of the process. We shall first examine the established regime of the sedimentometer operation, which is of the greater interest.

An exact value of the particular solution of Equation (1) may be found if the function P(t) is known. In analyzing this Equation we note that the law for the displacement of the pointer $\delta(t)$ will strictly agree with the law of the increase of the load in the cup, P, only in cases when $\delta' = \delta'' = 0$; $\delta' = \text{const}$, $\delta'' = 0$ and $\delta = A\delta' = B\delta''$. Therefore, theoretically exact operation of the sedimentometer is possible only in the following conditions:

$P = \text{const}$, as then $\delta' = \delta'' = 0$;
$P = At$, as then $\delta' = A$ and $\delta'' = 0$;
$P = Aa^{Bt}$, as then $\delta' = ABa^{Bt}$ and $\delta'' = AB^2a^{Bt}$.

Since the above laws for variation of the loads do not always hold in the sedimentometer, it is necessary to evaluate the magnitude of the error in the sedimentometer readings, which arises as the result of inertia motion of the beam and cup, and also of the resistance of the medium. From a knowledge of the law of variation of $\delta(t)$, determined by experiment, and by double graphical differentiation with respect to t, we obtain graphs for the functions $v = \delta'(t)$ and $a = \delta''(t)$, shown in Figure 3. Further, with a knowledge of the sedimentometer constants M_{fr}, l, I, M, K_2, K_1, Q and m, it is possible, from the graphs for $\delta'(t)$, $\delta''(t)$, and $\delta(t)$, to calculate the values and plot the graph for the required function P(t) according to Equation (1).

The constants l, M, and Q, were determined by direct measurement and weighing. For our sedimentometer they are: balance shoulder $l = 10$ cm; mass of the cup $M = 0.01394$ g·sec²/cm; weight of the beam $Q = 93.2$ g. The frictional moment M_{fr} was determined from the decrement of the decreasing vibrations of the beam and pointer; its value was 2.2 g·cm·sec² The coefficient of resistance to the motion of the cup in the viscous medium, K_2, was determined from the period of oscillation of the beam with the cup immersed in water ($K_2 = 0.0816$ g·sec/cm). The rigidity coefficient K_1 of the spring is found by calibration for different lengths of spring. For a spring length of 12.5 cm, $K_1 = 0.348$ g/cm. The distance m from the center of oscillation to the center of gravity of the beam was determined from the equilibrium of the beam at a definite load ($m = 0.055$ cm).

Examination of the graphs in Figure 3 and calculations according to Equation (1) with the method described above shows that the terms $\delta'(t)$ and $\delta''(t)$ in the Equation are very small in comparison with the term $\delta(t)$, and at their maximum value they are respectively 0.1 and 0.04% of the values of the term in the Equation containing $\delta(t)$, for the same time interval. The error of the microscope scale reading is 0.0002 g, which is several tens of times greater than the maximum values of the terms in $\delta'(t)$ and $\delta''(t)$.

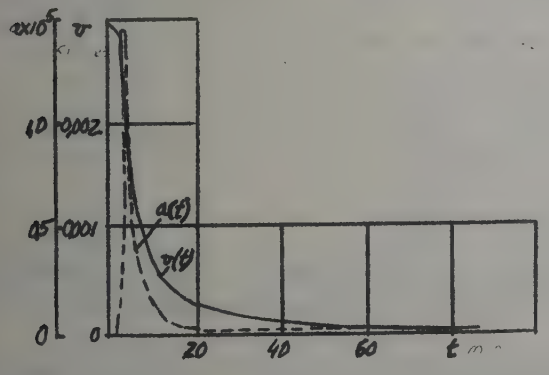

Figure 3. Change of the velocity v and acceleration a of the sedimentometer cup in the course of the analysis.

In investigations of peat suspensions of different degrees of dispersion, the ratios of the magnitudes given above may vary, but the order of magnitude remains the same. Thus, errors in the instrument readings due to the presence of inertia forces and the resistance of the medium are much less than the errors in the readings. It should also be noted that $\delta'(t)$ and $\delta''(t)$ have opposite signs and compensate each other. It follows that in practical calculations, the terms in $\delta'(t)$ and $\delta''(t)$ may definitely be neglected, and Equation (1) may then be written in the form:

$$P(t) = \left(K_1 + Q\frac{m}{l^2}\right)\delta(t) - \frac{M_{fr}}{l}. \qquad (2)$$

In sedimentometric analysis we are interested not in absolute values of P and δ, but only in the

changes ΔP and $\Delta\delta$ of these values in the course of the experiment. A condition of the accurate operation of the sedimentometer is

$$\frac{dP}{d\delta} = \text{const} = A, \tag{3}$$

which indicates that each change of the load in the cup corresponds, on a definite scale, to a change in the pointer reading, so that the law for the increase of the load in the cup corresponds to the law for the displacement of the pointer. Differentiation of Equation (2) with respect to t gives:

$$\frac{dP}{dt} = \left(K_1 + Q\frac{m}{l^2}\right)\frac{d\delta}{dt} \quad \text{or} \quad \frac{dP}{d\delta} = K_1 + Q\frac{m}{l^2} = \text{const}, \tag{4}$$

which was required to be shown.

Friction in the apparatus does not alter the law of the displacement of the pointer, as the value of M_{fr} does not enter Equation (4). The frictional moment of the sedimentometer is required to be constant in the course of the experiment, which can be always readily assumed in view of the small angles of displacement of the beam. The absolute value of the frictional force at the shoulder of the cup is one half of the error of the microscope scale.

Let us write Equation (4) in the form

$$d\delta = KdP \tag{5}$$

and designate the coefficient of sensitivity of the sedimentometer

$$K = \frac{1}{K_1 + Q\frac{m}{l^2}}. \tag{6}$$

Analysis of Formula (6) shows that the load sensitivity of the apparatus can be increased either by decreasing the rigidity K_1 of the spring or the restoring moment Qm of the balance, or by increasing the balance shoulder l. However, increase of the sensitivity of the apparatus should not lead to considerable changes of δ in the course of the experiment as small values of δ and φ are inherent in the correct operation of the sedimentometer.

Let us now examine transitional regimes of the sedimentometer operation. For this we find the general solution of the differential Equation (1), forming its characteristic Equation:

$$\left(\frac{I}{l^2} + 2M\right)r^2 + K_2 r + \left(K_1 + Q\frac{m}{l^2}\right) = 0, \tag{7}$$

hence

$$r = \frac{-K_2 \pm \sqrt{K_2^2 - 4\left(\frac{I}{l^2} + 2M\right)\left(K_1 + Q\frac{m}{l^2}\right)}}{2\left(\frac{I}{l^2} + 2M\right)}. \tag{8}$$

Investigation of the possible values of r shows that three cases are possible:

$$K_2^2 < 4\left(\frac{I}{l^2} + 2M\right)\left(K_1 + Q\frac{m}{l^2}\right);$$

$$K_2^2 = 4\left(\frac{I}{l^2} + 2M\right)\left(K_1 + Q\frac{m}{l^2}\right);$$

$$K_2^2 > 4\left(\frac{I}{l^2} + 2M\right)\left(K_1 + Q\frac{m}{l^2}\right).$$

As the value of the coefficient K_2 for water is very small, in practice the first case occurs most frequently in sedimentometric analysis. The third case is possible when the viscosity of the dispersion medium is high and the cup diameter is large, while the second is a boundary case.

Let us examine the first case, when the coefficient of resistance to the motion of the cup is fairly small. The general solution of the differential equation for this case is written in the form:

$$u = e^{\alpha t}(C_1 \cos \beta t + C_2 \sin \beta t), \tag{9}$$

as the roots of the characteristic equation (8) in this case will be complex, $r_{1,2} = \alpha \pm \beta i$.

Equation (9) is the equation for a damped vibratory motion which is superimposed on the basic motion of the sedimentometer cup under the weight of the settling particles of the suspension. Thus, the transitional regime of the sedimentometer operation when the viscosity of the medium is low is characterized by oscillatory movements of the pointer. The oscillations die down, as $\alpha < 0$ and when $t \longrightarrow \infty$, $e^{\alpha t} \longrightarrow 0$ and $u \longrightarrow 0$.

The duration of the transitional period, during which the oscillations of the pointer may affect the course of the sedimentometric analysis, may in general be theoretically determined from Equation (9). However, in practice the sedimentometer cup is always released from its initial position with a certain initial impulse due to the lifting of the balance and the descent of the cup into the liquid disturbed by stirring. Therefore, any calculation of the transitional period cannot be at all exact. The duration of the transitional period determined experimentally is about one minute, and is very small in comparison with the total time of the experiment, which lasts two or three days. The readings in the transitional period are taken from the central position of the pointer. The rapid damping of the oscillations is assisted by holding the free cup with the hand after the balance is raised, and by the resistance of the medium to the motion of the cup (which acts as a damper) immersed in the suspension. As Formula (9) shows, the duration of the transitional period is less as the coefficient

$$\alpha = \frac{K_2 l^2}{2(I + 2Ml^2)}. \tag{10}$$

is greater.

Consequently, to shorten the transitional period it is necessary to increase the diameter of the cup (K_2) and the shoulder of the balance l, or to decrease the moment of inertia of the beam, I, and the mass M of the cups.

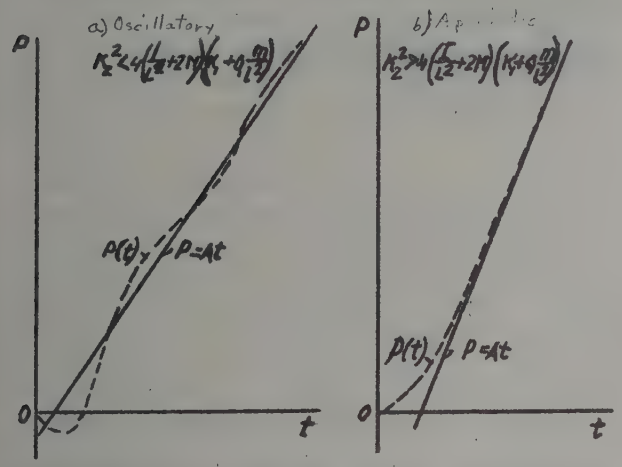

Figure 4. Graphs for the transitional regime of sedimentometer operation.

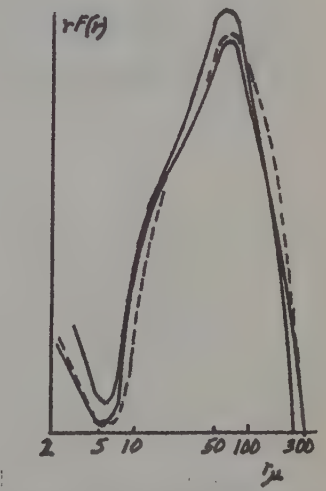

Figure 5. Distribution curves for peat suspension.

Let us now examine the case when $K_2^2 > 4\left(\frac{I}{l^2} + 2M\right)\left(K_1 + Q\frac{m}{l^2}\right)$, which corresponds to a dispersion medium of very high viscosity and cups of large diameter. The general solution of the differential equation (1)

$$u = C_1 e^{r_1 t} + C_2 e^{r_2 t} \tag{11}$$

will in this case be the equation for aperiodic motion superimposed on the basic motion of the cup under the weight of the settling particles. Figure 4 shows graphs for oscillatory and aperiodic transitional regimes superimposed on the straight line $P = At$, as at the start of the experiment the time dependence is as a rule linear. The graphs were obtained by solving the nonhomogeneous differential Equation (1), in which $P(t) = At$ was assumed.

From an examination of the transitional periods of the sedimentometer operation it may be concluded that they are of a very transitory, damped nature and do not have any appreciable influence on the course of the sedimentometric analysis. In addition, as the result of a number of measures (increase of the cup diameter, decrease of the moment of inertia, etc.), the transitional period may be shortened still further.

Figure 5 shows three distribution curves for the same peat suspension obtained with the aid of the sedimentometer described. The suspension was prepared from the < 0.25 mm fraction of complex-upper peat with 25% decomposition (hydromass with 96.8% moisture content after pumping hydro-peat). As Figure 5 shows, the distribution curves show good agreement. Thus the weight sedimentometer is a simple and accurate apparatus which is quite suitable for the sedimentometeric analysis of peat suspensions.

SUMMARY

1. A weight sedimentometer for the sedimentometric analysis of peat suspensions was designed and constructed.

2. The equation for the operation of the weight sedimentometer was derived and studied. As a result of the investigation it was established that the law of the displacement of the pointer corresponds, with an accuracy sufficient for practical purposes, with the law of the increase of the load on the sedimentometer cup. The transitional period of the sedimentometer operation has no appreciable effect on the course of sedimentometric analysis.

3. Repeated sedimentometric analyses of the same peat suspension gave results in good agreement.

The work was carried out at the suggestion and under the guidance of Professor M. P. Volarovich, to whom the author expresses his deep gratitude.

Moscow Peat Institute
Chair of Physics

Received September 16, 1953

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INVESTIGATION OF THE RHEOLOGICAL PROPERTIES OF DISPERSE SYSTEMS*

M. P. Volarovich

In the last few decades, rheology, the study of flow of substances, has been extensively developed. Since this is a new branch of science, its limits and content are not yet sufficiently defined. Rheology considers mainly the questions of deformation and flow of easily deformable materials, that is, the viscous flow of liquids, anomalous viscosity and plasticity of colloids, and also phenomena of relaxation, elastic after-effects and thixotropy in disperse systems.

At the present time rheological problems are met in every branch of industry. It is impossible to enumerate all the materials, the results of rheological study of which are applied in the technology of various industrial processes, and also in various constructional projects and calculations. As examples, the following may be indicated: clays, soils, peats, paints, lubricant greases, various petroleum products (oils, bitumens, etc.), high polymers, various construction materials (cement and lime suspensions, etc.) clay suspensions used in drilling, glues, resins, solutions of rubber, gelatin, and starch, various proteins (casein, etc.), fats and numerous other products of the food industry, various fibrous materials (silk, wool, artificial fibers, etc.), slags, glasses, refractories, and other fused silicates. In the Soviet Union rheology has been particularly widely developed in connection with the industrialization of the country and the mechanization of various production processes. For the design and utilization of various machines and mechanisms it is necessary to know the rheological properties of the materials which these machines process, transport, etc.

Rheology deals with processes associated with irreversible, residual deformations of matter. Consequently, it is a science contiguous with hydrodynamics and the theory of elasticity. Problems in the theory of elasticity are solved for reversible elastic deformations which do not depend on time and are of small magnitude. This is a first approximation to reality. In fact, absolutely elastic bodies do not exist. It is well known that all bodies which occur in nature in the natural state, and also all industrial products, have some measure of flow. The best kinds of elastic steel, if under sufficiently high stress, eventually show residual deformations caused by irreversible relative displacement of the particles of iron and carbon, that is, by flow of the substance. Such solids as stones and minerals also in many cases exhibit flow. The results of this are easily observed in mountains, where mineral strata become curved in a great variety of ways with the movement of the earth's crust as the result of plastic flow.

Rheology, a part of physical mechanics, was formulated as a separate branch of science quite recently, only 15-20 years ago. However, its foundations were laid gradually in the course of the preceding decades and centuries. In the process, rheology owes much to the fields of mechanics and the theory of elasticity, and also to viscosimetric methods. Famous Russian scientists — Lomonosov [1], Mendeleev [2], Petrov [3], Shvedov [4], Kurnakov [5] and others are the founders of the most important branches of rheology.

The present paper briefly gives the history of the development of studies in the field of rheology in Russia before the great October Socialist Revolution, and then describes a number of investigations by Soviet scientists on the rheological properties of disperse systems, the examples being taken mainly from the work of the author and his co-workers. The paper presents the phenomenological theory of viscoplastic flow of disperse systems, experimental work on the design of apparatus and development of methods of measurement of the rheological parameters of colloids, attempts at a colloido-molecular interpretation of viscoplastic flow of disperse systems, and also examples of the practical interpretation of the results of rheological investigations.

FROM THE HISTORY OF RHEOLOGY

The great Russian scientist M. V. Lomonosov, in developing his molecular-kinetic theory of the structure of matter, was interested in questions of liquid flow; he was the first to propose a capillary viscosimeter, a diagram

*Paper presented at the Conference on the Theory of Elasticity, Plasticity, and Rheology, at the Polish Academy of Sciences, August 27, 1953.

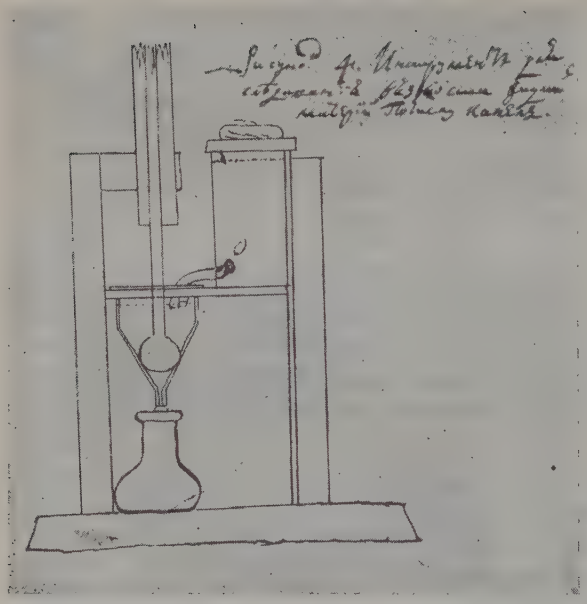


Fig. 1. Scheme of M.V.Lomonosov's capillary viscosimeter.

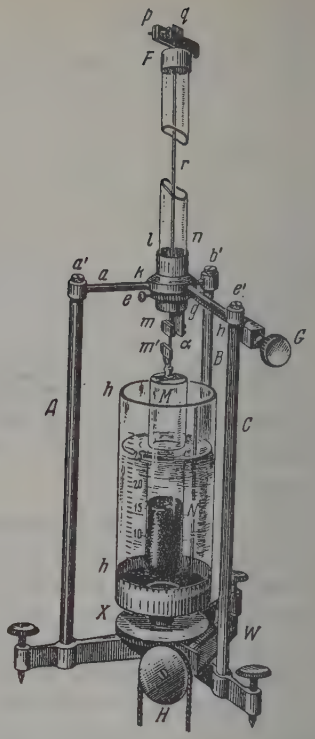


Fig. 3. F. N. Shevedov's rotational apparatus for investigating the elasticity of form and the anomalous viscosity of colloids (1889)

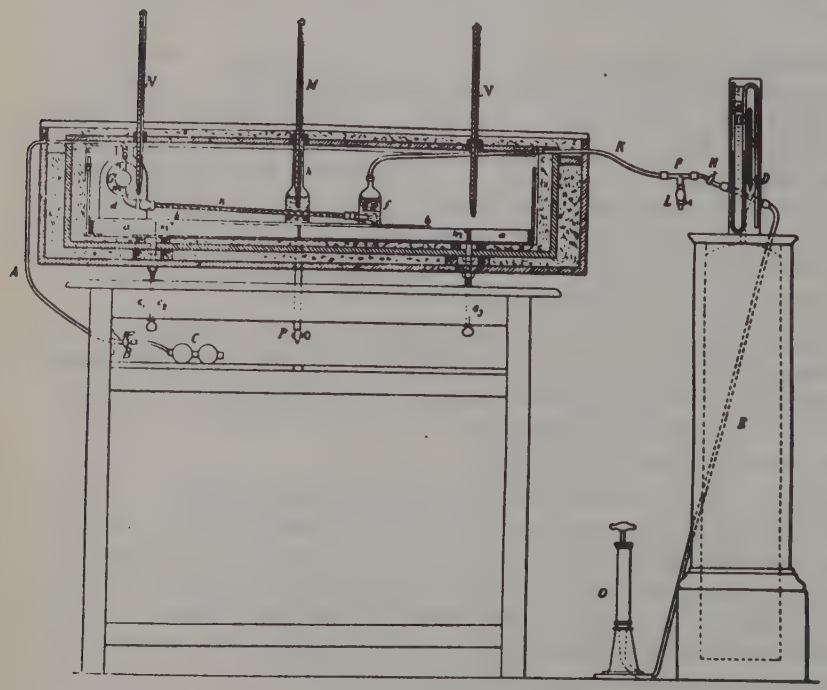


Fig. 2. Scheme of N. P. Petrov's capillary viscosimeter for the measurement of viscosity of lubricating oils in a wide range of temperatures (1885).

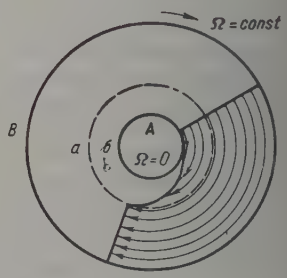


Fig. 5. Zones of elastic deformation (a) and plastic deformation (b) in a viscoplastic system which is in the space between two coaxial cylinders, the outer one of which rotates with an angular viscosity Ω.

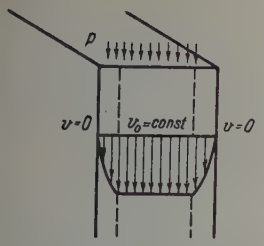
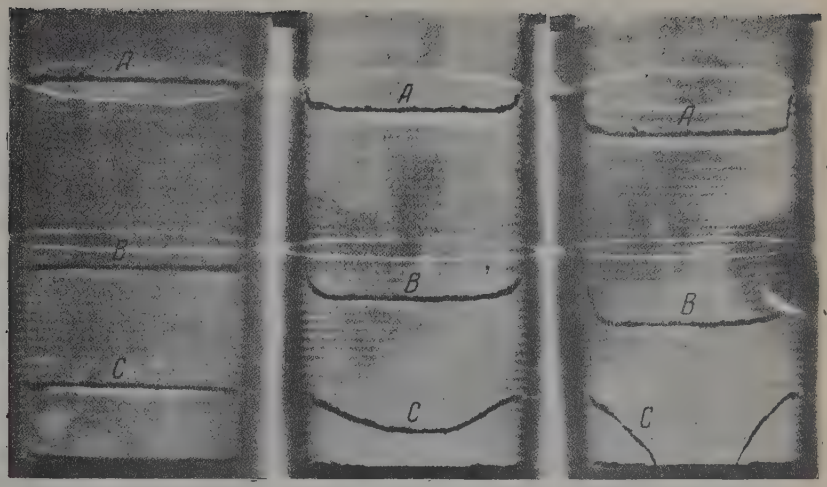


Fig. 6. Distribution of velocities in the flow of a viscoplastic system in a flat capillary under the action of pressure.



a b c

Fig. 8. X-Ray photographs of the flow of a lubricant grease in a round tube.

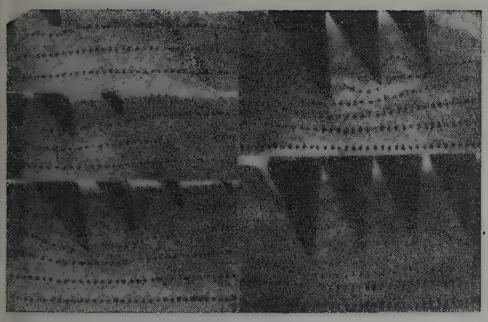


Fig. 9. X-Ray photographs of peat forming.

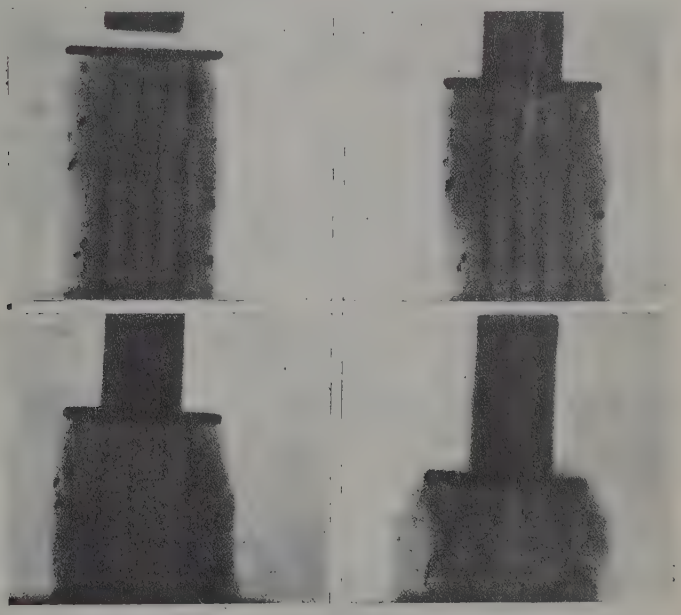


Fig. 10. X-Ray photographs of the squashing of a cylinder of viscoplastic peat. (Cinematography from an X-ray screen).

of which is shown in Figure 1. The principle of operation of the apparatus is clear from the sketch. In the directives of a meeting of the Committee of the Academy of Sciences on May 21, 1751 at which the decision was taken to construct a number of instruments for Lomonosov, this viscosimeter was termed "an instrument for the investigation of the viscosity of liquid substances by the number of drops".

It is interesting that Lomonosov proposed to measure the viscosity of liquids in connection with studies of "forces of cohesion" (of molecules) in liquids. He intended to study forces of cohesion both in pure liquids and in solutions, for example, "cohesion of alcohol drops", "cohesion of drops in presence of excess acid", "cohesion of bitumens". Thus, we see that Lomonosov was also concerned with questions of microrheology.

We will not deal with the generally known and most important work of the Petersburg academicians Daniel Bernouilli [6] and Leonard Euler [7] on the foundations of hydrodynamics of ideal liquids. We will also mention here the interesting work of Professor Gromeka [8] of the University of Kazan, which up to recent times was little known. Working in the field of hydrodynamics, Gromeka first introduced eddies in the equations for the motion of a liquid in the year 1891.

It is necessary to note the outstanding investigations of Mendeleev in 1880 [2] "on the resistance of liquids and on aeronautics". These studies by the talented chemist and physicist are not as widely known as his other remarkable work: the periodic law, etc. Examination of the work of Mendeleev on the flow of liquids shows that he paid much attention to the foundation of general principles of the hydrodynamics of viscous liquids. In his papers, devoted to a considerable extent to questions of aeronautics, he naturally made a fundamental examination of aerodynamic problems. However, he paid detailed attention to the important and at that time indefinite questions of the flow of liquids. In discussion of the question of the dependence of the resistance on the rate of flow of liquids, Mendeleev indicated quite correctly that at low rates of flow the resistance is proportional to the first power of the rate, and at high rates, to the square of the rate. We note that the paper by Reynolds [9] on laminary and turbulent flow regimes appeared later, namely in 1883.

The work of Mendeleev played an important part at the end of the last century on Russia in the development of many investigations in hydrodynamics, hydraulics, and aerodynamics, which really fall outside the limits of rheology (Zhukovsky [10], Chaplygin [11], and others), in the rheology of colloids (Shvedov [4] and others), and also in the rheology of lubricants (Petrov [3] and others). The famous Moscow engineer and physicist Zhukovsky stated in his paper at the 13th Conference of Russian Scientists and Doctors in Tbilisi in 1913 [12]: "D. I. Mendeleev indicated the path along which the development of difficult problems on the resistance of liquids should advance."

Petrov [3] is the founder of the hydrodynamic theory of machine lubrication; at the same time he laid the foundation of the rheology of lubricants. Petrov [13] designed and constructed a very accurate capillary viscosimeter, the scheme of which is shown in Figure 2. The oil under test, contained in the reservoir f, flowed through the capillary k into the bulb G under the action of the pressure set up in the manostat E by means of the pump O. The pressure was measured with the water manometer D. A seconds clock was used to measure the time to fill the bulb G with oil. The apparatus was placed in a thermostat, the temperature being controlled by three thermometers.

This apparatus of Petrov was the first absolute viscosimeter, which did not require preliminary graduation. In this connection, Petrov determined with great accuracy the dimensions of the capillary and the viscosimeter bulb, for calculating the viscosity by the Hagen-Poiseuille formula. Therefore, Petrov's results for the viscosity of water were no less accurate than Poiseuille's data [14]. Incidentally, an important difference between Petrov's viscosimeter and Poiseuille's apparatus is that Petrov had two reservoirs at the ends of the capillary. It has been necessary to refer to Petrov's viscosimeter because instruments of this type were afterwards frequently used in the USSR and other countries in investigations of the rheological properties of disperse systems.

Petrov determined the viscosity of some dozens of mineral and vegetable lubricating oils in the temperature range from 20 to 60°. He established that the degree of flatness of the viscosity-temperature curves is far greater for the latter than for the former. On the basis of these studies Petrov showed how lubricating oils may be chosen on a scientific basis for particular machines, and how to substitute one oil for another.

The significance of Petrov's work goes far beyond the limits of rheology of lubricants. At that time the problems of hydrodynamics were still very obscure, and there was no confidence in the applicability of the Navier-Stokes general equation for the motion of a viscous liquid to hydrodynamic and viscosimetric calculations. Petrov, who studied the extensive literature on theoretical and experimental hydrodynamics since the time of Newton (Euler, Bernouilli, Coulomb, Navier, Stokes, Meyer, Girard, Helmoltz, Jacobson, Poiseuille, Hagen, Mendeleev, and others), and analyzed and critically examined this extensive material, reached quite correct conclusions. He was the first

to show that Poiseuille's accurate experiments (for laminary flow of liquids in pipes) fully confirm the theoretical equations for the hydrodynamics of viscous liquids of Newton, Navier, and Stokes.

The founder of the rheology of disperse systems is Shevedov, who first demonstrated in his well-known papers [4] anomalous viscosity and elasticity of colloid form on the example of 0.5% aqueous gelatin solution. He showed that colloidal solutions, even of low concentrations, behave in flow not as normal truly viscous Newtonian liquids, but exhibit a limit of flow (limiting shear stress). This work of Shvedov is of very great interest and retains its primary importance.

The apparatus used by Shvedov, based on the principle of a rotating cylinder, is shown in Figure 3. The substance under test was placed between two coaxial glass cylinders, the inner one M of which was suspended from an elastic thread, while the outer one, hh could be rotated by an electric motor. By observations of the twisting of the elastic thread during uniform rotation of the external cylinder, it was possible to investigate the viscosity of the substance, while by rotation of the suspension head F with the outer cylinder M stationary it was possible to study the elasticity of form of the substance.

Shvedov determined the shear modulus G for 0.5% gelatin solution; its value was 0.535 dynes/cm^2. In a study of stress relaxation processes for this solution Shvedov showed that Maxwell's equation of relaxation [15] does not satisfy the experimental data; the stresses do not vanish completely, and Shvedov therefore introduced an additional term in Maxwell's equation. The relaxation time T for the gelatin solution in question was found to be 13.7 sec.

Thus, Shvedov was the first to observe in colloidally disperse systems those anomalous effects which are usually graphically represented as shown in Figure 4, a. The abscissa axis of this Figure represents the moment of rotation M; and the ordinate axis, the angular velocity of rotation of the cylinder of the rotational viscosimeter. In agreement with the integration of Newton's equation, obtained by Petrov, namely

$$\eta = K\frac{M}{\Omega},$$

where η is the viscosity of the liquid and K is a constant for the apparatus, calculated from its dimensions, the graph for $\Omega = f(M)$ is linear for truly viscous liquids (see line A in Figure 4, a). For colloidal solutions and coarsely disperse systems the dependence of Ω on M is curvilinear, as shown by line B in Figure 4, a. It is seen from Figure 4, b that in such a case the anomalous viscosity η_a for colloidally disperse systems has a variable value, which decreases with increase of the shear stress τ, or, which is the same thing, with increase of the velocity gradient. The viscosity η of normal Newtonian liquids naturally does not depend on the stress and rate of shear. It should be stressed that experiments with capillary viscosimeters lead to the same laws.

Examining the results of his experiments, Shvedov was the first to write the equation for steady viscoplastic flow of a substance. He wrote this equation in the following form:

$$\eta_a = GT + \frac{\Theta}{\dot{\gamma}}, \qquad (1)$$

where η_a is the anomalous (variable) viscosity; Θ is the limiting shear stress; $\dot{\gamma}$ is the rate of shear, or the velocity gradient. The value of η_a may be substituted by $\frac{\tau}{\dot{\gamma}}$, as the anomalous viscosity was calculated as the ratio of the complete shear stress τ to the velocity gradient. Further, in agreement with Shvedov and with Maxwell it may be assumed that the product of the shear modulus G and the relaxation time T is equal to the true viscosity of the medium η_{pl}, which is now termed plastic viscosity. Then

$$\frac{\tau}{\dot{\gamma}} = \eta_{pl} + \frac{\Theta}{\dot{\gamma}}, \qquad (2)$$

and finally the equation for the viscoplastic flow of a substance may be written:

$$\tau - \Theta = \eta_{pl}\frac{dv}{dz}, \qquad (3)$$

the velocity gradient $\dot{\gamma}$ being denoted by $\frac{dv}{dz}$.

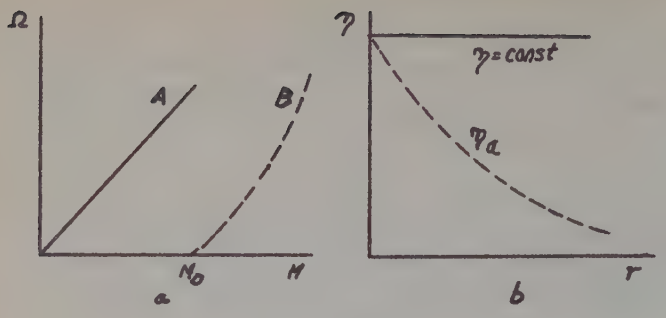


Fig. 4. Graphs for anomalous viscosity of disperse systems: ---- normal Newtonian liquid; — · · · · disperse systems with anomalous viscosity.

The existence of a limiting shear stress Θ (limit of flow) in colloidally disperse systems is shown by graphs of the type shown in Figure 4, a. The point of intersection of the curve B with the abscissa axis (M_0) shows that at moments of rotation less than M_0 no flow takes place in a viscoplastic system. The value of Θ is easy to calculate knowing M_0, as M_0 is a simple function of Θ.

If it is assumed that Θ = 0, or that the substance has no limit of flow, Equation (3) becomes Newton's usual equation for viscous flow.

Shvedov's pupil, Professor Veinburg [16] in 1912 integrated for the first time Equation (3) for the case of a viscosimeter with a rotating cylinder. Veinberg also studied the rheological properties of ice [17]. Together with a number of co-workers he also published a series of papers on the rheological properties of bitumens [18]; in this work he developed a number of new instruments and methods.

Later Equation (3) received wide application in the rheology of disperse systems. It was derived by Bingham and integrated by Buckingham for the flow of a viscoplastic medium in a circular pipe [19]. Gutkin and the author showed [20] that the system of equations of Hencky [21] and also of Ilyushin [22] describes the properties of the same type of viscoplastic medium as does Equation (3).

Related to Shvedov's work are Demets' studies of the mechanical properties of liquids and colloidal solutions, in particular his observations of flow birefringence [23]. On the other hand, the work of Gezekhus on elastic after-effects in rubber [24] stands a little apart.

Steady Flow of a Viscoplastic Substance

The Shvedov-Bingham Equation (3) for viscoplastic flow is fairly easily solved for a number of cases. It has therefore been repeatedly subjected to experimental verification on various disperse systems. In many cases satisfactory results were obtained.

According to the Equation (3) for plastic substances, flow, associated with irreversible deformations, commences only when the stresses exceed the limiting shear stress Θ. At stresses less than Θ, only elastic deformations may be observed. This definition of plastic flow agrees to a considerable extent with that given in qualitative form by Maxwell [25]. It should only be noted that at shear stresses less than Θ, real bodies may exhibit phenomena of kinetic elasticity, that is, elastic after-effect processes.

However, for cases of steady flow such deformations may nearly always be neglected, as they are small. On the other hand, residual viscoplastic deformations in disperse systems are usually very great, which is highly characteristic of the rheology of easily deformable materials.

Theoretical Solutions. Returning to Equation (3) we note that, in addition to the above-mentioned examples, namely tubes of circular section [19, 26] and the relative rotation of coaxial cylinders [16, 27, 28], it was integrated for the following cases: a longitudinally displaced cylinder [29], a cylinder being flattened [30], flow through slit and annular capillaries [20—1946, and 31], flat flow of two viscoplastic masses in contact [32], rotation of a roller in a bearing for the case of a viscoplastic lubricant [20—1947], flow along an inclined plane [33, 34]. Naturally, in the more complex cases the differential equations for the flow of a viscoplastic liquid had to be written in the more general form according to Hencky and Ilyushin [20, 21, 22].

In solving problems of this type it is always necessary to bear in mind that a viscoplastic substance which is under stress in the process of flow may have regions both of plastic and of elastic deformation. In regions of elastic reversible deformations only, the stress does not reach the limiting shear stress. Conversely, in the regions of plastic deformations the stresses exceed the flow limit, and in these regions irreversible flow of the substance occurs.

One of the fundamental problems both of theoretical and of practical rheology is the definition of these regions or zones. Figure 5 shows the zones of elastic deformations a and plastic deformations b for the case of a

viscoplastic substance in the gap between two coaxial cylinders A and B, one of which (in the present case, the external one B) rotates at a constant angular velocity Ω. This case was examined theoretically and also studied practically [28].

Figure 6 shows a scheme for velocity distribution in the case of flow, under a pressure p, of a viscoplastic substance through a flat capillary, that is, through a narrow slit of rectangular section. The middle portion of the mass, analogously to that in a pipe of circular section, moves as a solid body at a constant velocity v_0.

The cases were also examined when the limiting shear stress Θ or the plastic viscosity η_{pl} were variable along the axis or the radius of the pipe for a viscoplastic disperse system flowing in a pipe of circular or annular section [35]. This may occur when part of the dispersion medium (for example, water in the case of peat) is filtered off through the porous walls of the pipe. Attempts were made to solve the problem of the fall of a sphere in a viscoplastic medium [36], but a correct solution was not obtained [34].

There are attempts to develop a similarity theory for the viscoplastic flow of a substance [30, 37, 38] and to establish the corresponding similarity criteria. Work in this important direction must be extended and broadened. For cases of flow of a viscoplastic disperse system (clay suspension) in pipes, a generalized Reynolds criterion was proposed, which includes the limiting shear stress [37].

It must be emphasized that one of the peculiarities of viscoplastic flow of disperse systems—easily deformable materials—which distinguishes them from metals, minerals, rocks and similar "solids", the plasticity of which has been considered in a number of works [39, 40, 41, 42, 43], consists of very great viscoplastic deformations with high velocities during their flow.

The problems cited above have a definite practical significance. The solutions obtained are either used in calculations of the values of Θ and η_{pl} in the experimental determinations of these quantities for various disperse systems in capillary and rotational viscosimeters, etc., or are used in calculations of various cases of flow of disperse systems and in project development of various technological processes [44-52].

EXPERIMENTAL METHODS AND APPARATUS

It is necessary to devote some attention to the methods and apparatus used in rheological investigations of colloidal and coarsely disperse systems. The aim of experimental investigations of methods is the design of apparatus and the development of methods for the determination, with its aid, of the rheological parameters: Θ, η_{pl}, relaxation time, characteristics of elastic after-effects. Rheological apparatus and methods are very diverse, which is due to the great variety of real liquids and disperse systems, and also of their practical flow conditions. It must not be thought that one or two instruments will suffice for all cases of rheological measurements on liquids and disperse systems. For materials of different consistencies, for different stresses and velocity gradients, different apparatus must be used. Instruments which give arbitrary characteristics (Engler type viscosimeters, penetrometers, farinograph for dough testing, etc.) should not be used in rheology, and they will not be discussed here; they were critically reviewed in a number of our papers [50, 53].

It must be stressed that the correct choice of apparatus and technique in many cases is not simple, but in the field of rheology it is particularly important in order to ensure success. We may refer here to two historical examples: as was indicated above, Lomonosov [1] was the first (in 1751) to propose the use of a capillary viscosimeter (steady flow) for the measurement of viscosities of liquids, and this is the basic viscosimetric method at the present time; Coulomb [54] later (in 1798) devised a viscosimeter based on the principle of torsional vibrations (nonsteady flow) but this apparatus now has hardly any applications in viscosimetry.

Rheological methods and apparatus may be divided into the integral and the differential, and also into apparatus with homogeneous and heterogeneous fields of stresses and deformations.

1. Integral methods—capillary and rotational apparatus, etc.—make it possible to observe the total effect of flow, namely: the volume of liquid passing through the capillary in unit time, at a definite pressure, the angular velocity or the number of turns of the cylinder per second under the action of a given load in the rotational viscosimeter, etc. For substances with anomalous viscosity and plasticity it is particularly important to use integral methods with homogeneous stress and deformation fields, as interpretation of the observations is then much simpler. In such cases simple shear occurs in the whole volume of the disperse system.

It is important that the working parts of the apparatus should be simple, so that the solid surfaces between which the substance under test is placed should give simple boundary conditions, and also that the treatment of the observations should not be complicated. The latter is very important for apparatus for large scale tests, in particular, for factory laboratories.

The following are integral methods with homogeneous or almost homogeneous fields of stresses and deformations:

a) Rotational, single linkage types of apparatus with a rotating cylinder: Shvedov [4], Volarovich [55, 56], Rebinder and co-workers [57], Vinogradov and co-workers [58], Trapeznikov [59], and others. In these instruments the field is close to homogeneous when the gap is narrow. Rotational double linkage types (Gorazdovsky [60]) with a homogeneous field, with the working parts consisting of two semi-tores of special shape, or in the form of two conical rings. The rotational double linkage apparatus of Tolstoy [61], with rings, with a field close to homogeneous.

The Volarovich rotational viscosimeter RV-4 has been applied to the determination of the limiting shear stress Θ and the plastic viscosity of concentrated disperse systems (clays [28], paints [55], lubricant greases [63], peat [64], suspensions of building materials [65], etc.).

The RV-7 rotational viscosimeter [56] is used for highly viscous liquids and disperse systems, in particular for lubricating oils in the region of low temperatures down to $-60°$ [51, 66], for bitumens at high temperatures up to 180° [67], for printing inks, etc.

b) Instruments with longitudinal displacement of some body: tangential shear of a horizontal plate placed on a cube of the substance under test (Veinberg [68], Tolstoy [69]), longitudinal displacement of coaxial cylinders (Tolstoy [29], Volarovich [70], Velikovsky [71]) between which the system under test is placed (if the gap is small, the field is close to homogeneous), longitudinal displacement of a vertical plate pulled out of a vessel with the substance tested (Rebinder and Veiler [72]) when the field is close to homogeneous; all the three methods based on longitudinal displacement are applied for relatively small deformations and deformation rates.

Integral nonhomogeneous methods include:

a) Capillary type instruments. These were used for lubricants by Velikovsky [71], Kusakov [73], Vinogradov [74], Fuks [51, 75], Ramaiya [76], P. I. Sanin [45], and others; for rubber solutions, by Dogadkin [77], for peat by Volarovich and Kulakov [78], etc.

b) The cone immersion method which, after the work of Rebinder, Yampolsky, and Semenenko [79] received a theoretic basis and can be applied to the determination of limiting shear stress in disperse systems; it was used by Volarovich and Markov [80] for low humidity peat.

c) The ball fall method, used for peat, which, as Kulakov showed [81], is not to be recommended for disperse systems.

d) The vibrational method, which is also not recommended for rheological investigations because of its nonsteady character.

2. Differential methods permit the direct observation of deformation in the course of time at every point in the disperse system during flow, so making it possible to establish the field and velocities of deformation, and sometimes also the stress field. In this case the homogeneity condition is not so important, although it is also very desirable. It is important that these methods permit the investigation of complex cases of flow of disperse systems.

Differential, nonhomogenous methods:

a) Velocity distribution may be observed on the surface of a disperse system in an apparatus with a rotating cylinder (see Figure 5; Volarovich and Tolstoy [28]; Fuks [82]); the zones of plastic deformations, and also of elastic deformations when the stresses do not exceed the limiting shear stress, are well defined.

b) The velocity profile in flow in pipes was determined by Volarovich, Kulakov, Samarina, Semensky, and Bezzubov [83] for a peat mass by the electrical contact method both in laboratory conditions and in peat factories, with pipes up to 750 mm diameter. The velocity profile for lubricant greases extruded from tubes was studied by an optical method by Volarovich, Tolstoy, and Loshakova [84].

c) To study fields of deformation and deformation velocities in the liquid for opaque objects, in particular for flow in pipes, we developed a method of X-ray transmission, which has found application in the study of kinematics of flow of disperse masses in mechanical models: worm conveyors, cones, etc. (Volarovich, Gorazdovsky, Lazovskaya, Markov [80, 85].

d) Division of elastic and plastic zones in the flow of partially crystallized melts of minerals by observation of the orientation of crystals in polished plates prepared after tempering (observed microscopically by Volarovich and Korchemkin [86]).

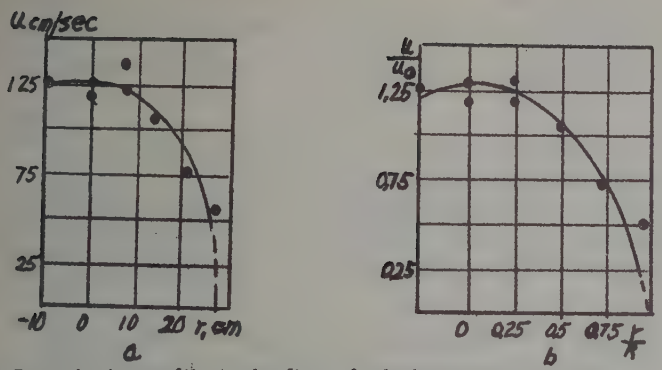


Fig. 7. Velocity profile in the flow of a hydrous peat mass in a pipe 570 mm diameter, established experimentally by observation of closing of a circuit between probe electrodes.

e) Vinogradov [87] developed a method of microcinematography, in particular in polarized light, for the process of flow of lubricant greases in a flat capillary. The method is suitable for microcrystalline transparent substances and makes possible the determination of the stress field.

f) A special type of double measurement method was developed by Kusakov and Kislinsky [88]; with this method it is possible, in one experiment, to plot the temperature dependence curve of the viscosity of a lubricating oil by observation of the rate of fall of a small sphere in the oil in a steady field of variable viscosity, which is due to differences in the temperatures at the top and bottom of the cylinder.

Figure 7 shows, as an example, an experimentally determined velocity profile for the flow of a peat suspension with a moisture content of about 95% in a pipe of 57 cm diameter [83]. Figure 7, a shows the dependence of the velocity u on the distance r to the axis of the pipe, and Figure 7, b shows the same profile in dimensionless coordinates, R being the radius of the pipe and u_0 the average flow velocity of the mass.

Figures 8, 9, and 10 show, as examples, results obtained in studies of the flow of disperse systems by the X-ray transmission method [85]. Figure 8 shows the flow of a lubricant grease in a pipe of circular section. The consecutive photographs a, b, and c, taken at intervals of 5 and 10 minutes, show that deformations of the grease occur only near the tube walls; in the center the strips A and B of barium sulfate are not deformed at all. The central portion of the grease, where the shear stress is less than the limiting value Θ, moves, in accordance with the theory of viscoplastic flow, as a continuous "solid" cylinder. At the lower end there was a round orifice with diameter about one third that of the tube diameter, and the grease flowed out through this. As a result, deformation of the strip C has a peculiar character. In particular, Figure 8 c clearly shows "dead" zones near the sides of the tube, where the grease does not flow.

Figure 9 shows four consecutive X-ray photographs taken by the author together with Markov, which show the process of forming of moist peat by a so-called forming caterpillar. It is seen from Figure 9 that as the forming apparatus descends, deformations spread through the peat. In the last stages of the process the motion in the depth of the mass is oscillatory in nature.

Figure 10 shows the results obtained by the X-ray transmission method with the use of cinephotography. The process of squashing a viscoplastic peat cylinder was studied. The cinephotography from the X-ray screen was at the rate of eight frames per minute. The four photographs in Figure 10 were chosen from the cine-film at intervals of 30 frames. By this method rapid deformation processes can be studied.

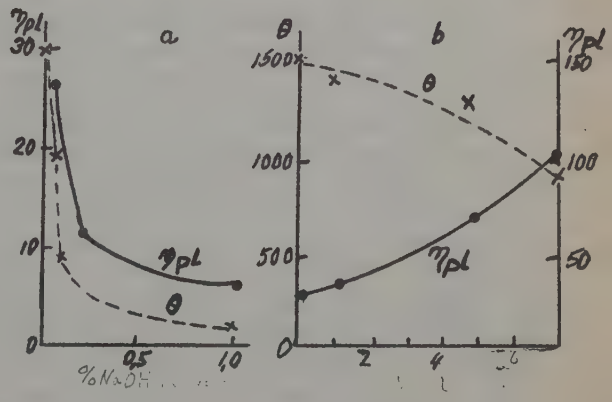


Fig. 11. Dependence of the limiting shear stress Θ and plastic viscosity η_{pl} on the addition of electrolytes, for Glukhovets kaolin with 55% moisture.

Differential, homogeneous methods:

a) The methods of observations described under "a", "c", and "e" of the previous section can naturally be also applied for cases of flow with homogeneous fields.

b) Tolstoy's apparatus [61] with flat rings (see integral homogeneous methods) may also be used as a differential method.

c) The blowing-off method (Deryagin and Kusakov with co-workers [89]) is used for the study of volume anomalous viscosity properties of lubricants (transparent materials) in thin layers contiguous with a solid wall.

d) Tolstoy [69] developed the apparatus with a tangential displacement of a horizontal plate also as a differential method.

It should be noted that at the solid walls of rheological instruments in contact with disperse systems slippage may occur, as a layer of the dispersion medium is often formed on such walls. Nevertheless, the solutions of problems of viscoplastic flow according to Equation (3) are carried out under such boundary conditions when the substance adheres to the solid surfaces. Petrov [3, 13] examined the question of the possibility of slippage of liquids on solid walls. It may, however, be assumed with very great accuracy that slippage of liquids on solid surfaces does not usually occur.

To avoid slippage of disperse systems, the solid surfaces of rheological instruments (cylinder, plates, etc.) may be made with a roughened surface, which in many cases leads to good results [28, 29, 55, 69, 72]. In many cases the slippage effect of a disperse system may be excluded by theoretical calculations in viscosimetric observations [3, 47, 78, 81, 90]. Wall slippage of disperse systems and also of true liquids was studied in detail by Tolstoy [69, 90].

EXAMPLES OF RHEOLOGICAL STUDIES OF DISPERSE SYSTEMS

The parameters of a viscoplastic substance in Equation (3), namely the limiting shear stress Θ and the plastic viscosity η_{pl}, permit the structure of disperse systems to be studied. A series of papers by Rebinder [91] and his co-workers are devoted to these questions of microrheology. The different microrheological significance of these two parameters Θ and η_{pl} for viscoplastic flow is seen from the graphs shown in Figure 11, taken from the paper by Volarovich and Tolstoy [92]. As is seen from Figure 11, a, addition of NaOH, which peptizes the suspension, considerably lowers both Θ and η_{pl}; on the other hand, the addition of NaCl, which causes coagulation, only slightly decreases Θ and at the same time increases the plastic viscosity of the suspension. An attempt to calculate the thickness of a layer of vaseline in a suspension of colloidal mica [62], which ensures the existence of a limiting shear stress, gave a value of the order of one micron, which is in fairly satisfactory agreement with the thickness of thin liquid layers of anomalous viscosity, according to Deryagin's investigations [89, 93].

For various disperse systems only one of the two parameters Θ and η_{pl} plays the principal role. For such highly viscous materials as bitumen, the limiting shear stress often plays a secondary part, while the important part is played by the viscosity, which reaches tens and hundreds of thousands, and even millions of poises and over [67].

Conversely, in many disperse systems with a dispersion medium of low viscosity, in particular in aqueous suspensions, the principal role is played by Θ, which is a very characteristic parameter of such systems. This was shown in a number of cases for lubricant greases with a low viscosity base by Rebinder [94] and Velikovsky [95].

Tsarevich and Malyshev [96] proposed a formula for flow of clay suspensions in pipes, which includes only the limiting shear stress, on the basis of the fact that pressure losses in pipes depend mainly on Θ, and as a first approximation are independent of the plastic viscosity of clay suspensions. An analogous formula was derived by the author [83] for the flow of a hydrous peat mass, with a dry content from 8 to 2%, in pipes. Velocity profile experiments in pipe ducts from 44 to 75 mm diameter confirmed that pressure loss depends very little on the plastic viscosity of suspensions and solutions, but is determined by the value of the limiting shear stress of the hydrous mass. For constructional suspensions (lime, etc.), the value of η_{pl} for which is great, it was shown by the work of Lobanov [65] that the Buckingham formula [19, 26] should be used; this includes both the parameters of viscoplastic flow, both the plastic viscosity and the limiting shear stress.

For peat of decreased moisture content, with a water content of from 92 to 75%, the limiting shear stress is a very characteristic value [64]. In particular, Lazovskaya [97] showed that when the moisture content of peat falls from 83 to 79%, its limiting shear stress Θ becomes 3 times as great, while η_{pl} increases to a small extent, only by 15-20% (Figure 12). It was found as a result that the dependence of total flow of peat on pressure when it flows in a conical nozzle [97] is determined by the value of Θ, and it is practically independent of η_{pl}. In addition, Markov and the author [80] were able to establish that the limiting shear stress may very conveniently be used to characterize the degree of processing of peat in various processing equipment, since this is associated with destruction of its structure.

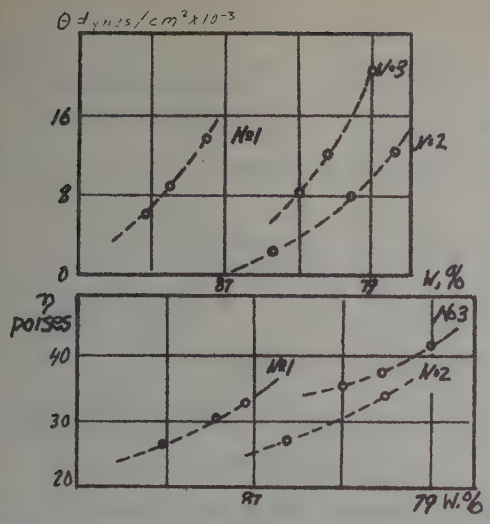


Fig. 12. Dependence of the limiting shear stress of peat and its plastic viscosity η_{pl} on the water content, from data obtained with the RV-4 rotational viscosimeter.

In other studies a connection was found between the structural and rheological properties of adhesives and the strength of the adhesive film [98]. It was established that when rubber is dissolved after mastication, the viscosity of the solutions is considerably less than the viscosity of solutions of unmasticated rubber, while the limiting shear stress Θ of the solutions becomes zero. At the same time the strength of the adhesive film in the case of masticated rubber is 50% less than for unmasticated rubber. The explanation for these effects is that mastication changes the structure of the rubber molecules, the molecules being broken down and the molecular chains becoming shorter. These changes destroy the solution structure, as a result of which Θ decreases to zero, and the strength of the adhesive film correspondingly falls.

In this paper we did not examine the important kinetic elastic phenomena which occur in disperse systems and high polymers at stresses less than the limiting shear stress Θ. Such investigations, which continue the work of Shvedov, were extensively developed in the laboratories of Rebinder [57, 99], Kargin [44], Vinogradov [58, 74], Trapeznikov [59, 100], Velikovsky [95], in our laboratory [50, 53, 101], and others.

In conclusion we must briefly touch on investigations of thixotropic phenomena in disperse systems. In steady viscoplastic flow of a system in the region when the Shvedov Equation (3) is valid, thixotropy is practically excluded, as the thixotropic structure of the system is usually already completely destroyed. In a series of experiments we carried out a preliminary destruction of the thixotropic structure by mixing before measurement of Θ and η_{pl}, which can be very conveniently done in the rotational viscosimeter. However, in the study of kinetic elastic phenomena in disperse systems at small shear stresses thixotropic processes introduce many complications.

A special study of thixotropic effects may be carried out in two ways: either by observations of the restoration of the structure of a system after its preliminary complete destruction by mechanical means, or by observations of the destruction process during mixing at a gradually increasing velocity gradient $\frac{dv}{dz}$, or, which is the same thing, during increase of the shear stress τ. In both cases the strength of the thixotropic structure of the system may conveniently be characterized by the limiting shear stress. The first method was successfully applied by Rebinder and Segalova [57] with their co-workers. From these experiments it was possible to draw a number of conclusions concerning the presence of condensational or dispersional structures in various disperse systems.

The second method was developed by Volarovich and Valdman [66, 102, 103] for lubricating oils in the low temperature region with the use of the RV-7 rotational viscosimeter. It was found that network types of thixotropic structures of paraffins, formed in lubricating oils on cooling, are very unstable. These systems are to a great extent thixolabile, and in any case restore their structure slowly. The limiting shear stress which appears in lubricating oils after cooling disappears completely when such a system is mechanically stirred. Thus, while having anomalous viscosity after cooling, oils become truly viscous Newtonian liquids after isothermal mixing with a destroyed structure and at low temperatures. In this connection, in calculations for the commencement of movement of a piston in an engine cylinder at low temperatures [104] it is necessary to take into account the limiting shear stress of the lubricating oil; in further movement, only the viscosity of the oil should be considered, as the structure of the oil is already destroyed. In the steady movement of a roller in a bearing at low temperatures, as was shown in our experiments [105], the usual equations of the hydrodynamic theory of lubrication may be applied.

The above examples show how the results of rheological investigations of disperse systems are applied for practical purposes.

Received February 19, 1954.

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